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ISOTOPE ANALYSIS FOR LEAD AND SULPHUR  
FROM THE GREAT SLAVE LAKE AREA

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
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"WHAT SEE'EST THOU ELSE IN THE DARK BACKWOOD  
AND ABYSM OF TIME?"

Prospero the Magician in the "Tempest"



## ABSTRACT

A survey of the isotopic composition of lead in a number of mineral samples from the Slave Province has been completed. The project originated with several objectives in mind. A primary objective was to develop mass spectrometric techniques to the point where precise, reproducible data could be obtained on a routine basis. In addition, an efficient method of purifying galena samples and extracting trace leads from other minerals with a minimum of contamination was investigated. These objectives have been realized. At present the method is able to reproduce ratios to within 0.2%. Much precision was gained through the use of a digital voltmeter to print both the peak height and baseline ten times per second to five figures. As the time between runs is lessened, the solid-source data will be nearly as precise as gas-source data with the advantage of no spurious peaks at masses other than (208, 207, 206, 204), tailing, or contamination due to complex chemical procedures.

Several trial runs were made with the Yellowknife samples until meaningful data was obtained. It was found that Slave Province has a rather more complex history than indicated by K-Ar data. It seems to have formed over a long period of time with several stages of magmatic differentiation adding material to it and altering the pre-existing rocks.

Two major orogenic events were dated, one at 2860 million years corresponding to the construction of Slave Province and one at 1550 million years corresponding to the construction of Churchill Province. The anomalous lead line also indicated an event at 4070 million years. The lead ratios for some samples collected at Pine Point dated at 270 million years which is 100 million years younger than the host rocks containing the lead. Sulphur isotope ratios have been analyzed as well.



## ACKNOWLEDGEMENT

The samples for this thesis were collected by Dr. G. L. Cumming and Dr. R. E. Folinsbee; the instruments were kept running by Dr. H. R. Krouse and much good advice was given by Dr. E. R. Kanasewich.

Much thanks is owed to Dr. Cumming for his encouragement when no results seemed to be forthcoming after several months of work, and for his good recommendations which resulted in adequate financial support for the author while research was in progress. Thanks also goes to Dr. Baadsgaard whose effective chemical procedures and suggestions always resulted in perfect emission, and to Dr. Sasaki for the preparation of samples for sulphur analysis.

The sulphur data were run at the suggestion of Dr. Krouse who was often hunting for leaks in the  $\text{SO}_2$  system with the author until the early hours of the morning. I would like to especially thank Dr. Krouse for the many hours he spent in his laboratory, with and without the help of the author, working to get the best results possible from the mass spectrometer.



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## INTRODUCTION

This thesis deals primarily with the lead isotope ratios for a specific area. Before presenting the data, however, it shall deal briefly with the theory used to set up models used to explain the data. Then a discussion of the theory of continental growth in Chapter II and the theory as applied to the thesis area in Chapter III shall prepare the reader for the actual presentation of the data in Chapter IV. A need for much additional research is suggested in the interpretation. Suggestions for future research are set out in Chapter V.



## CHAPTER I

## LEAD ISOTOPE ABUNDANCES

THEORY

Although relative chronologies may be derived from geological and paleontological data, an absolute chronology is one based on a process that has been active throughout geological time. As yet, we have been dealing only with relative chronologies based on geological observations or dating methods whose validity may be in question due to the disturbing effect of extreme temperature. Therefore it is desirable to find a process which has produced measurable effects at a constant rate independent of such phenomena as temperature, pressure, magnetic fields or cosmic ray bombardment. Furthermore, it is desirable to find a method especially applicable where paleontological, stratigraphic, and geological evidence is non-existent. The subject of this thesis, "Isotope Analysis", is the only method. Chapter I shall deal briefly with the basic theory behind this method and some probable histories a lead mineral may have in the earth before it finally finds its way into the laboratory. Various models shall be discussed and in Chapter IV, the data already gathered shall be fitted to one or more of these models. It is hoped that the usefulness and validity of this method in dating events of even a very complex geological history shall be demonstrated.

Discussion of these models involves the various terms used to describe lead depending upon its history. Natural lead may be classified as follows:

Primeval Lead

It was formed when the Earth was formed. The time at which it existed is referred to as time " $t_0$ ", the age of the Earth.





### Common Lead

It is lead which has no U, Th associated with it at the present time and only one U/Pb environment. A single-stage lead.

$$\text{Common Lead} = \text{Primeval Lead} + \text{Radiogenic Lead}$$

### Conformable Lead

That which is deposited, free of contamination, at the same time as its host rocks.

### Anomalous Lead\*

This is defined as "lead in which the isotope ratios were produced in two or more distinct lead-uranium systems, as opposed to common leads which were formed in a single lead-uranium system".

In this section, the theory behind the simple models used to explain ordinary lead abundances will be discussed first. A discussion of the more complex models used to explain anomalous leads will follow.

To make the simple model a few basic assumptions must first be made.

(1). All the leads were originally derived from a homogeneous source. As it is unlikely that the rocks of the upper crust could be considered homogeneous enough; only the mantle remains as a possible source. Furthermore, since there has been no evidence put forward as yet to contradict the suggestion that the U, Th concentration of the mantle is fairly high, that suggestion has been accepted as valid. Therefore, one may say that nuclides have been decaying throughout geologic time and adding Radiogenic lead to the primeval lead already in the mantle.

---

\* Russell, Ulrych, and Kollar - Nature, 1961.



(2). At some time "t" the lead was differentiated from the mantle and deposited in some mineralizing event in the upper crust. No radiogenic lead was added after the time of mineralization.

This model is called a single-stage model. Radiogenic lead was formed from the time "t<sub>0</sub>" when the earth formed until the time "t" when mineralization occurred. The growth equation may be expressed in the form

$$N = N_0 e^{\lambda t} \quad (1)$$

N is the number of atoms of the isotope present at time "t". Time in this case is counted into the past so that the present is designated as t = 0. At time t = 0 the number of atoms present is N<sub>0</sub>.

For the closed single-stage system in which we are interested the number of Pb<sup>206</sup> atoms present at time "t" is:

$$N(Pb^{206})_t = N(Pb^{206})_{t_0} + N(U^{238})_{t_0} - N(U^{238})_t \quad (2)$$

If the equation is divided through by the amount of Pb<sup>204</sup>, then in terms of the symbols defined (Table I) Equation (2) becomes:

$$x = a_0 + 137.8 V_0 (e^{\lambda t_0} - e^{\lambda t}) \quad (3)$$

Similar expressions may be written for the Pb<sup>207</sup>/Pb<sup>204</sup> and Pb<sup>208</sup>/Pb<sup>204</sup> ratios for a particular sample.

$$y = b_0 + V_0 (e^{\lambda' t_0} - e^{\lambda' t}) \quad (4)$$

$$z = c_0 + W_0 (e^{\lambda'' t_0} - e^{\lambda'' t}) \quad (5)$$

These equations form the growth curves for ordinary leads.

The accepted constants for these growth curves are given in Table I and have been used in this thesis.

Equations (3), (4) and (5) are applicable only in the case of a constant specified value for V<sub>0</sub>, W<sub>0</sub>. The general case is expressed below:



TABLE I  
BASIC GROWTH CURVE PARAMETERS

RATIO	PRESENT	TIME "t"	TIME "t <sub>o</sub> "
Pb <sup>206</sup> / Pb <sup>204</sup>	a	x	a <sub>o</sub>
Pb <sup>207</sup> / Pb <sup>204</sup>	b	y	b <sub>o</sub>
Pb <sup>208</sup> / Pb <sup>204</sup>	c	z	c <sub>o</sub>
U <sup>238</sup> / Pb <sup>204</sup>	137.8 V <sub>o</sub>	137.8 V <sub>o</sub> e <sup>λt</sup>	137.8 V <sub>o</sub> e <sup>λt<sub>o</sub></sup>
U <sup>235</sup> / Pb <sup>204</sup>	V <sub>o</sub>	V <sub>o</sub> e <sup>λ't</sup>	V <sub>o</sub> e <sup>λ't<sub>o</sub></sup>
Th <sup>232</sup> / Pb <sup>204</sup>	W <sub>o</sub>	W <sub>o</sub> e <sup>λ''t</sup>	W <sub>o</sub> e <sup>λ''t<sub>o</sub></sup>

#### CONSTANTS\*

137.8 V <sub>o</sub> = 8.99 ± 0.07	a <sub>o</sub> = 9.56	λ = 0.1537
W <sub>o</sub> = 35.55	b <sub>o</sub> = 10.42	λ' = 0.9722
t <sub>o</sub> = 4.55 × 10 <sup>9</sup> yr.	c <sub>o</sub> = 30.00	λ'' = 0.0499

#### BASIC ASSUMPTIONS

- (1) At Time "t<sub>o</sub>" all lead had the same ratios a<sub>o</sub>, b<sub>o</sub>, c<sub>o</sub>.
- (2) The amount of Pb<sup>204</sup> in the Earth is always constant.
- (3) No U, Th is associated with lead after time "t".
- (4) Lead isotopes are chemically identical.

---

\* Kanasewich



## METHODS OF DATING GALENAS

THE HOLMES, HOUTERMANS METHOD

The parameter  $V_o$  may be eliminated by dividing (4) by (3)

$$\omega = \frac{y - b_o}{x - a_o} = \frac{e^{\lambda' t_o} - e^{\lambda' t}}{137.8(e^{\lambda t_o} - e^{\lambda t})} \quad (6)$$

Since the age of the Earth,  $t_o$ , is a constant, then for a particular time "t" the quantity "w" is a constant. Plots of y vs x will give a straight line of slope w through  $a_o$ ,  $b_o$ . This equation is known as Houtermans "isochron equation". The primeval abundances of lead are assumed known, as is the value " $t_o$ ". (See Fig. 1).

Values of x, y from the mass spectrometer are plotted on the curve and time "t" is read. For all ordinary leads the isotope ratios should fall on the growth curve calculated from equations (3), (4) and the values given in Table I.

THE RUSSEL, FARQUHAR, CUMMING METHOD \*

This method assumes a homogeneous source with  $V_o$ ,  $W_o$  constant in the mantle. At time  $t = 0$  (the present) equations (3,4,5) give:

$$a = a_o + 137.8 V_o (e^{\lambda t_o} - 1) \quad (7)$$

$$b = b_o + V_o (e^{\lambda' t_o} - 1) \quad (8)$$

$$c = c_o + W_o (e^{\lambda'' t_o} - 1) \quad (9)$$

which if substituted back into 3,4,5 give:

$$x = a - 137.8 V_o (e^{\lambda t} - 1) \quad (10)$$

$$y = b - V_o (e^{\lambda' t} - 1) \quad (11)$$

$$z = c - W_o (e^{\lambda'' t} - 1) \quad (12)$$

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\* Russell and Farquhar: Lead Isotopes in Geology.







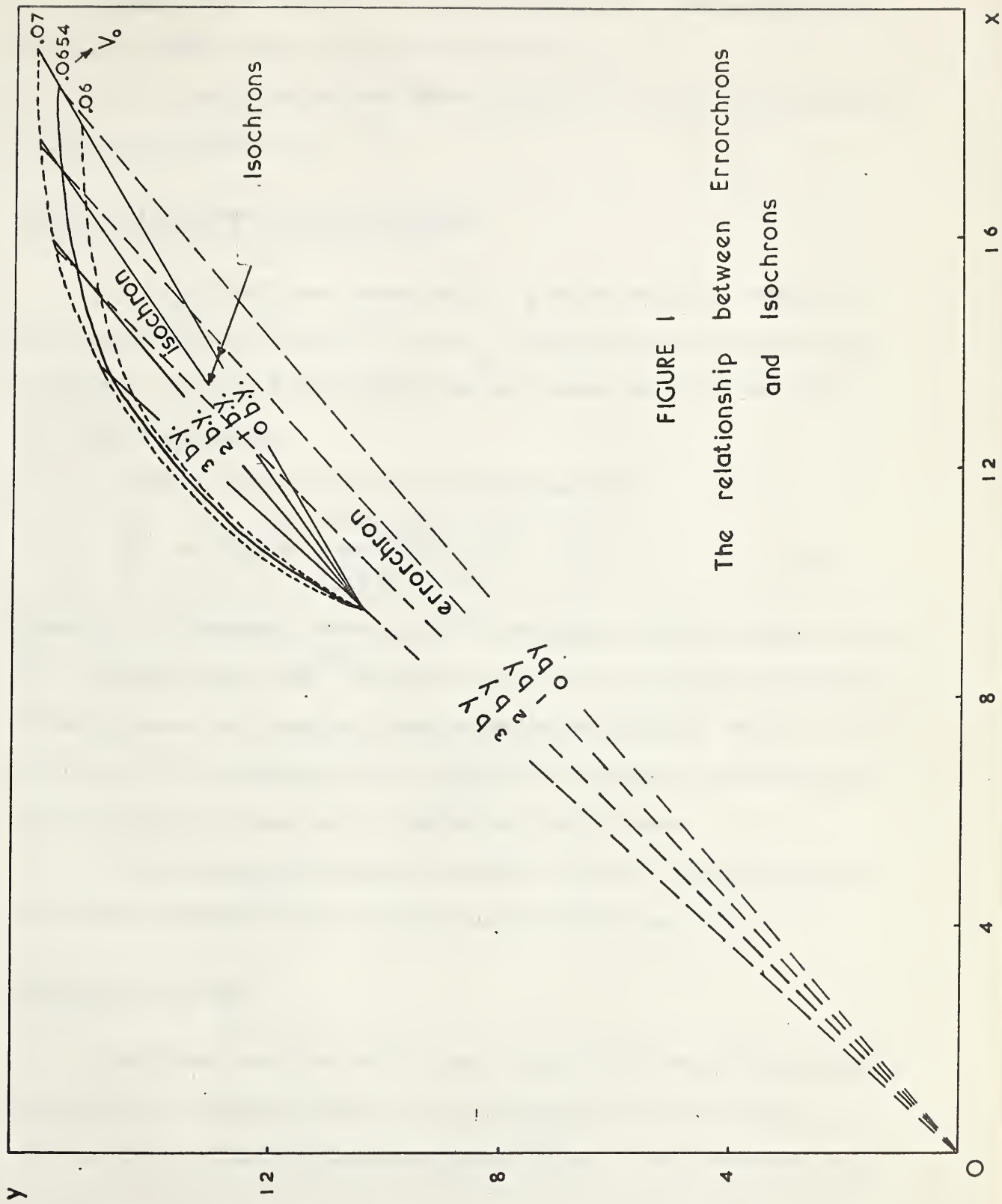


FIGURE 1

The relationship between Errorchrons  
and Isochrons



These may be evaluated if we know the present day isotopic ratios  $a, b, c$ , and  $V_o, W_o$  without knowing the age of the Earth or  $a_o, b_o$ .

The ratios determined from ordinary lead should fit the growth curves shown in Figure IIa and Figure IIb.

#### RUSSELL-STANTON-FARQUHAR METHOD\*

A single growth curve connecting  $a_o, b_o$  to the present day values  $a, b$ , may be constructed utilizing the  $a, b$ , and  $t_o$  values found from an analysis of meteoritic data. Only the leads satisfying the basic assumptions will fit this model. (i.e. conformable leads).

Equations 10 and 11 may be combined to produce

$$\frac{x}{y} = 137.8 \frac{(a/137.8 V_o - e^{\lambda t} + 1)}{(b/V_o - e^{\lambda' t} + 1)} \quad (13)$$

Equation 13 is independent of errors in  $Pb^{204}$  determination and is a function of time "t". In Figure 1 errors in  $Pb^{204}$  measurement may be corrected for by plotting "Error-chrons" as shown. An isotope ratio may be extrapolated along the "errochron" to the growth curve. This technique applies if and only if the leads are conformable ordinary leads which have developed in a single Lead-Uranium system.

If a consistent set of constants is used the Houterman's "isochron" formula and the Russell-Farquhar formula will give nearly identical age values.

#### MULTISTAGE MODELS\*\*

Multistage models are usually used to explain the existence of anomalous leads which may be derived from any of several possible sequences of events:

(I) It was removed from the homogeneous mantle at time "t" and incorporated into

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\* Russell and Farquhar - Lead Isotopes in Geology.

\*\* Kanasewich - Lead Isotope Abundances - Ph.D. Thesis.



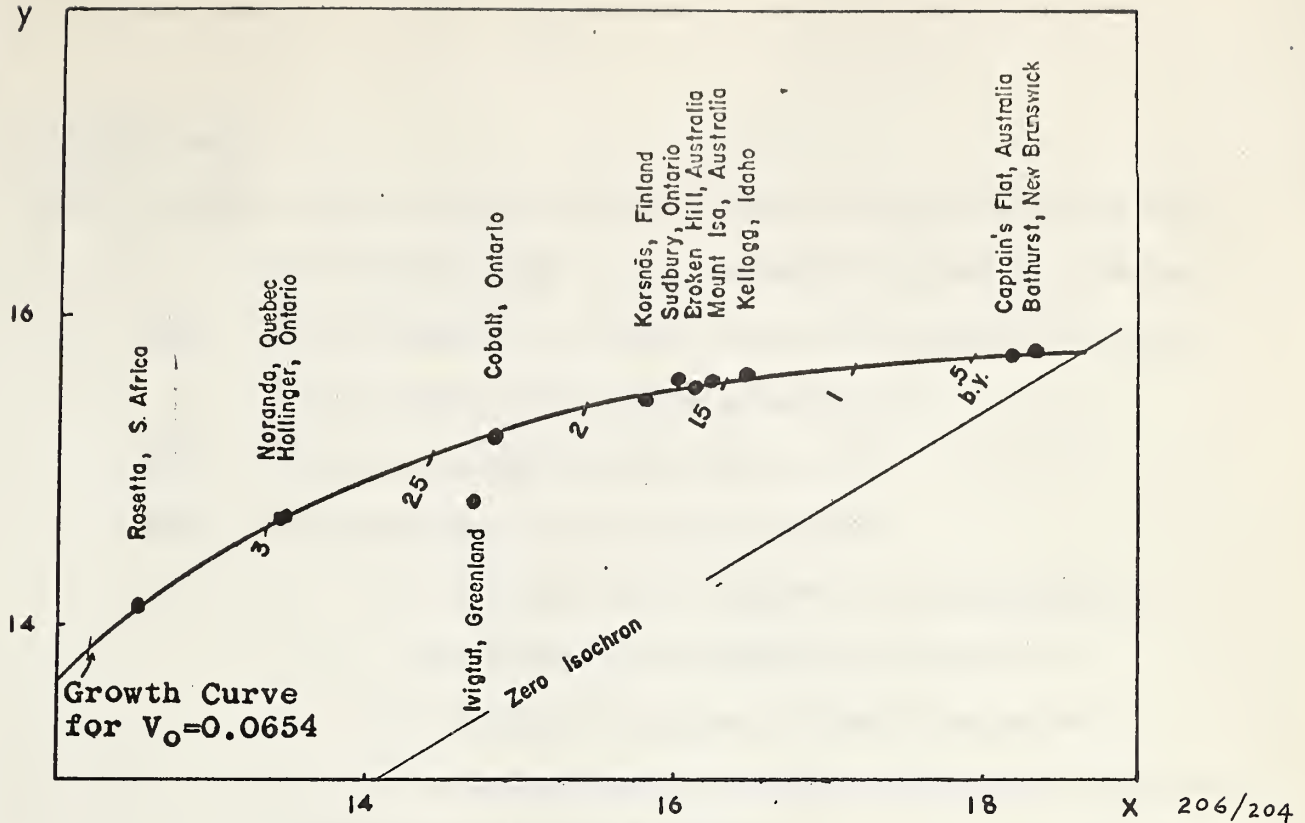


FIGURE II a

The relationship between  $x$  and  $y$  for some common leads.

which appear to satisfy  
criteria for a single-stage  
model.

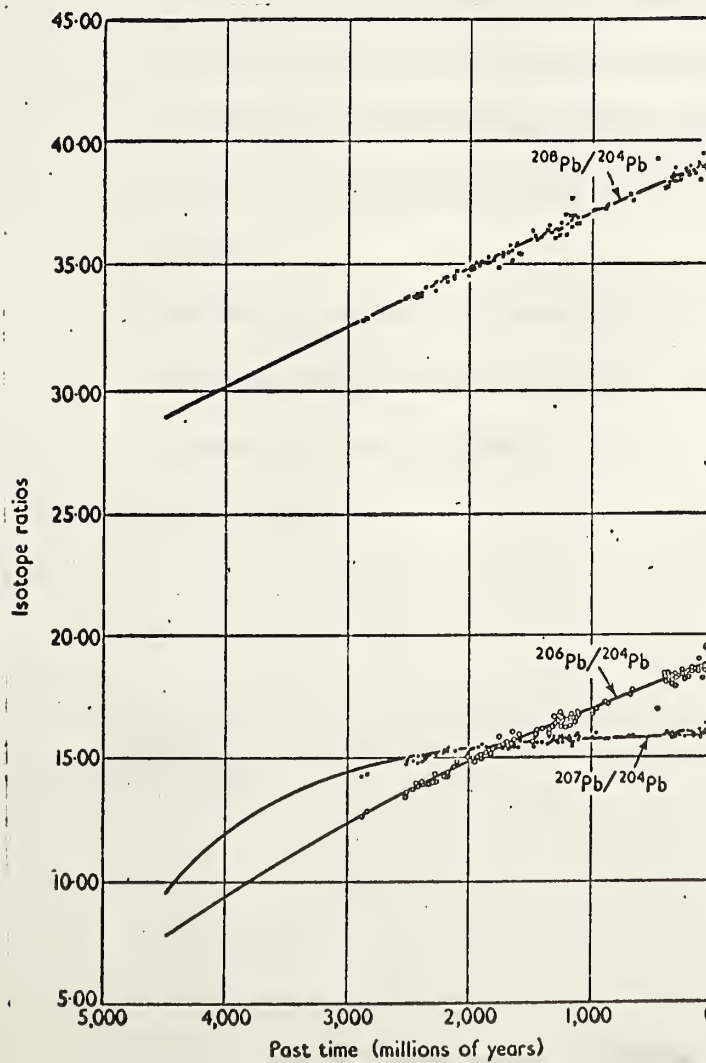


FIGURE II b

Growth curves for lead  
shown as a function  
of time.

From Russell and Farguhar  
"Lead Isotopes in Geology"





the crustal rocks.

THEN: (EITHER) It was incorporated into an environment of the same U, Th composition as the mantle, so is indistinguishable from lead in the mantle.

(OR) It was incorporated into crustal rocks of low or high U, Th concentration and grew along different growth curves.

(OR) It was incorporated into rocks with no U, Th.

(OR) It was remobilized at a later time and either

- a. rehomogenized to the growth curve corresponding to the average U, Th content of the crustal rocks.
- b. mixed with lead present in older or younger rocks.
- c. mixed with lead extracted from the mantle at a later date.

Assume a model\* of the following characteristics

(1) Lead has grown from primeval lead along growth curve OA (Fig. III).

At pt. A it is still common lead of ratios  $x, y$  at time  $t_1$ .

(2) At time  $t_1$  uranium is introduced into the system or the lead is mineralized into a uranium-rich (or Uranium-deficient) system. The growth curve in this system may be AC or AD. where AB is the mantle growth curve.

(3) At time  $t_2$  the lead is isolated from the uranium environment and the ratio may end up at point C or D. The slope of line CBD corresponds to time  $t_2$ . (See equations)

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\* A two-stage model.





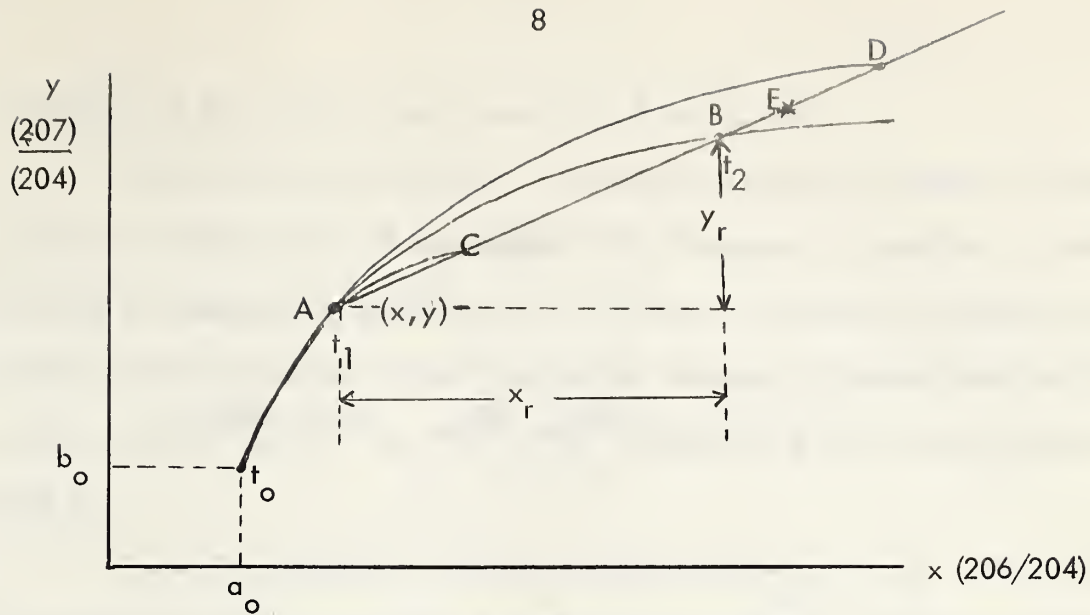


FIGURE III A MULTISTAGE MODEL

If appreciable amounts of radiogenic lead ( $x_r, y_r$ ) are produced between times  $t_1$  and  $t_2$  then anomalous leads of composition ( $x_a, y_a$ ) will be produced.

$$x_r = 137.8 k V_o (e^{\lambda t_1} - e^{\lambda t_2}) \quad (14)$$

$$y_r = k V_o (e^{\lambda' t_1} - e^{\lambda' t_2}) \quad (15)$$

$$x_a = x + x_r \quad (16)$$

$$y_a = y + y_r \quad (17)$$

If the U, Th concentrations in the crustal environment ( $KV_o$ ) ( $KW_o$ ) are variable ( $K_n V_o$ ) ( $K_n W_o$ ) each  $K_n V_o$  will produce a different growth curve all of them terminating at time  $t_2$  where

$$w = \frac{y_a - y}{x_a - x} = \frac{e^{\lambda' t_1} - e^{\lambda' t_2}}{137.8 (e^{\lambda t_1} - e^{\lambda t_2})} \quad (18)$$

which is an equation similar to (6) which is Houterman's isochron equation. Usually  $K > 1$  for acid rocks and  $K < 1$  for basic rocks.  $w$  gives a slope corresponding to a straight line passing through  $(x, y)$  and  $(x_a, y_a)$  called an anomalous lead line.

### Case I.

If at time  $t_2$  a very intense mineralizing event mixes and rehomogenizes all these leads free of contamination by leads mineralized at a time other than " $t_1$ " then they will tend to cluster about a point on the growth curve corresponding to the



average value  $KV_o$  of the crystal rocks. (Pt. E on Fig. III).

Often in a case like this  $K = 1$  and we get a lead which appears ordinary on the  $y$  vs  $x$  plot since Pt. E approaches Pt. B. However, it is possible to identify this lead as anomalous by observing the  $z$  vs  $x$  plot. In this plot the difference in chemical behavior between U and Th under the influence of thermal stress usually results in the  $Pb^{208}/Pb^{204}$  vs.  $Pb^{206}/Pb^{204}$  ratios falling far off their growth curve.

#### Case II.

If, on the other hand, lead mineralized at time  $t_2$  is mixed with lead which has mineralized at time  $t_1$  an isochron plot will emerge with a slope which also intersects the curve at times  $t_1$  and  $t_2$ . It will not be easy to tell if Case I or Case II has occurred. It may be expected for Case II that few ratios will fall above the growth curve, since it is a mixture of two ordinary leads which formed at times  $t_1$  and  $t_2$ . Of course, it is possible for a combination of the two possibilities to occur.



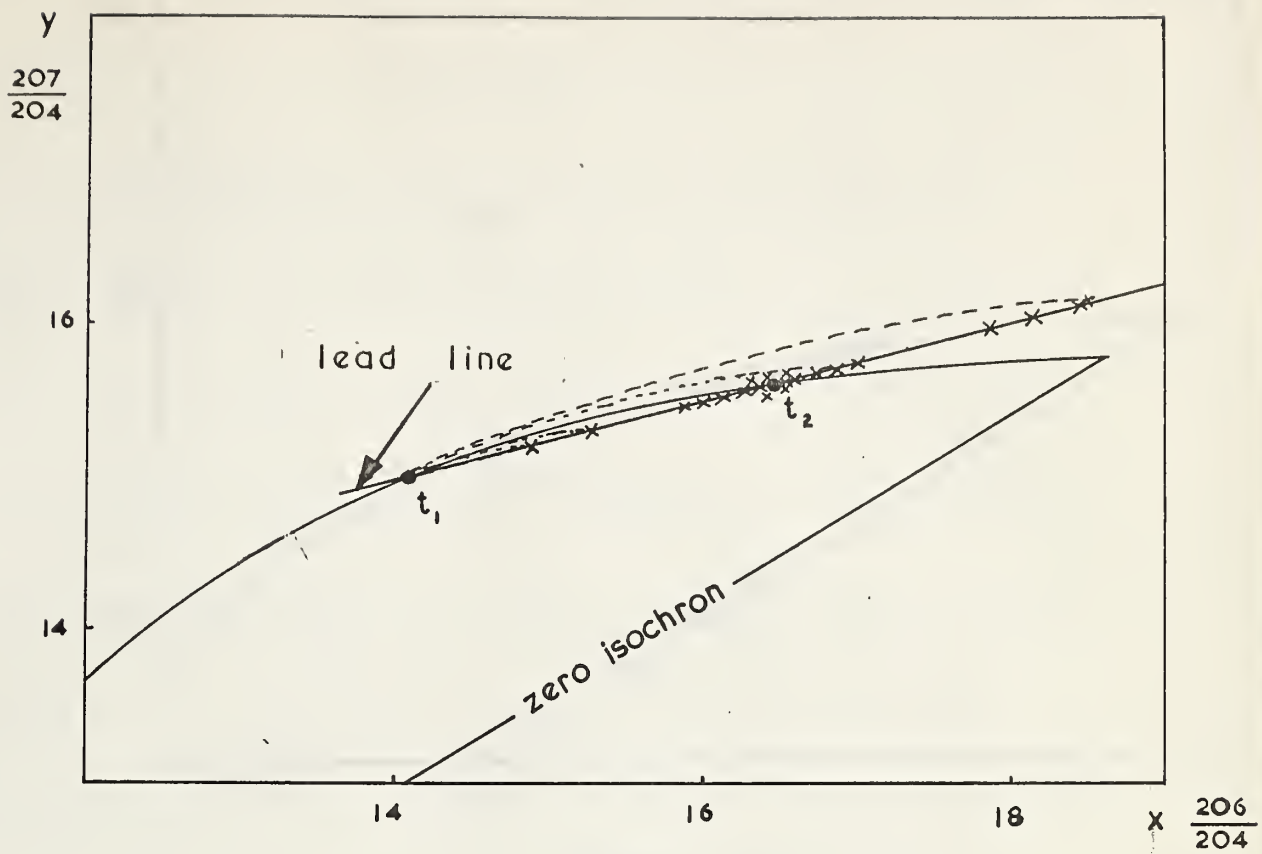


FIGURE IV a

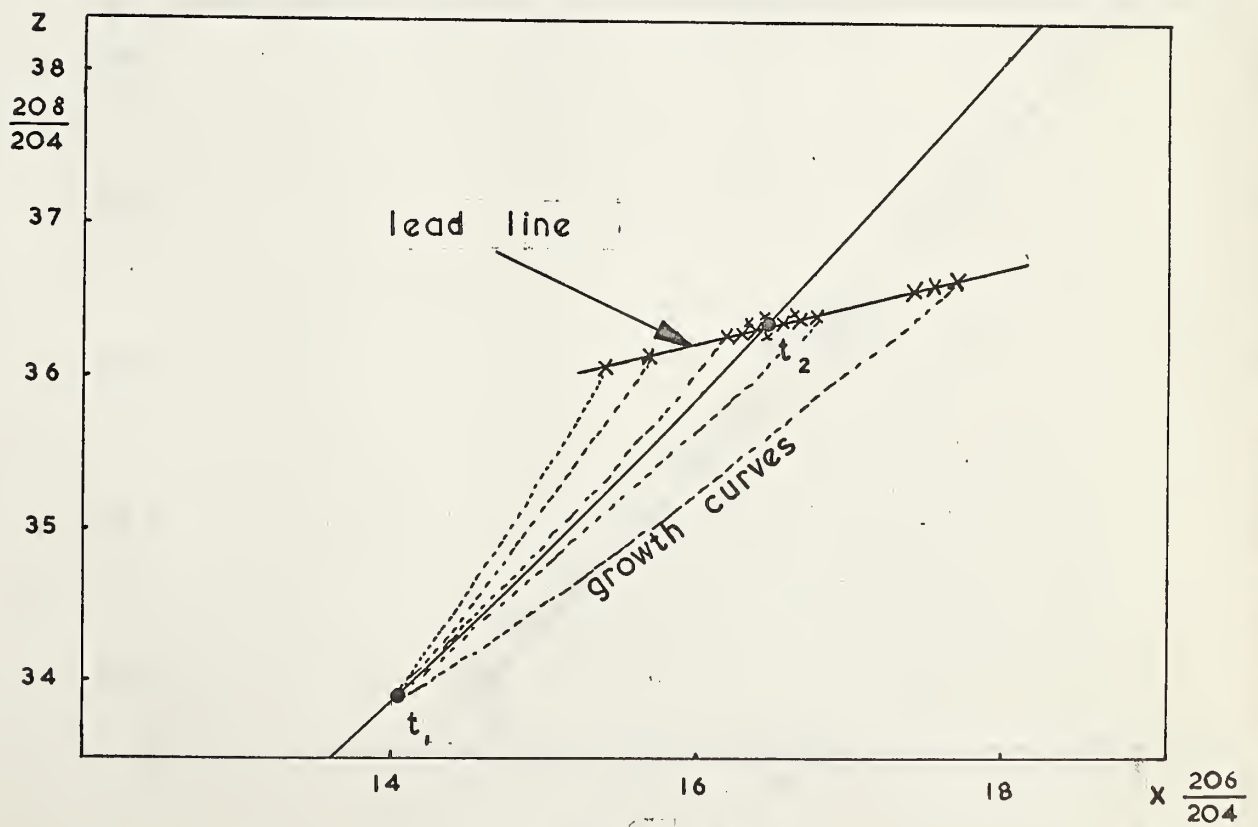


FIGURE IV b

CASE I Growth in crust followed by rehomogenization



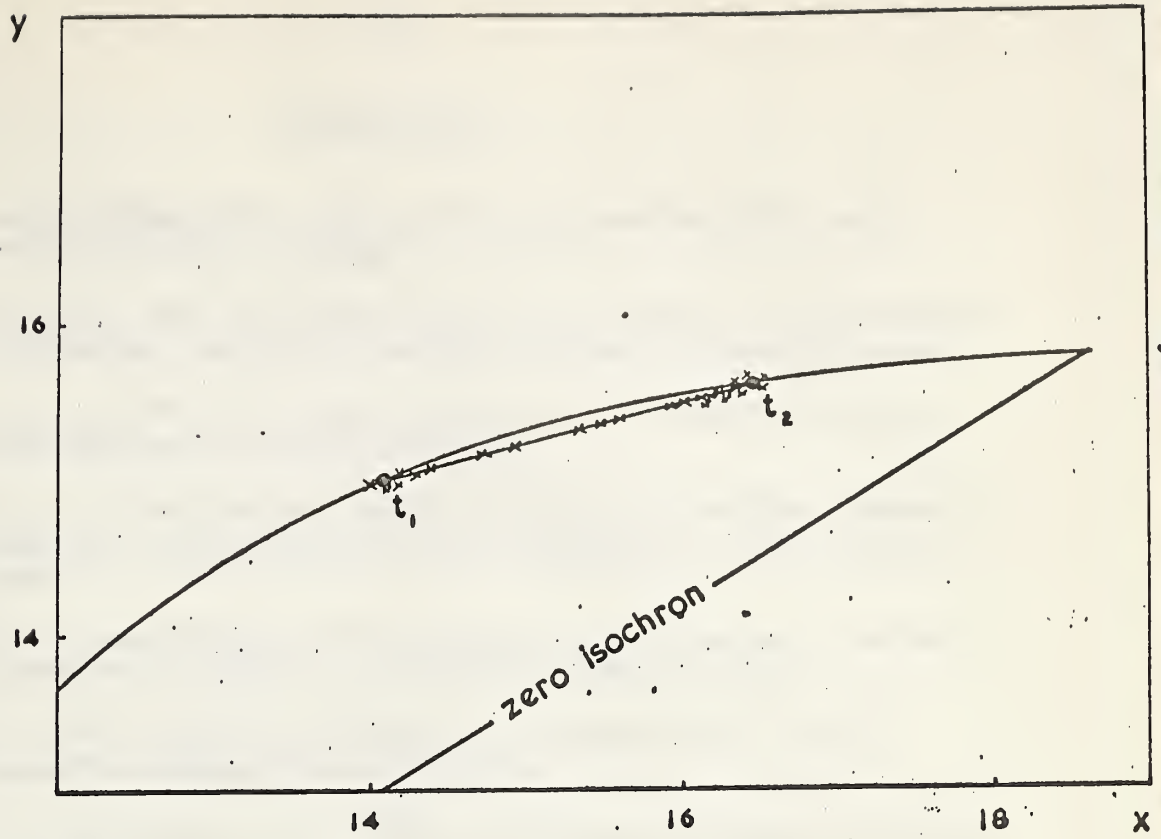


FIGURE Va

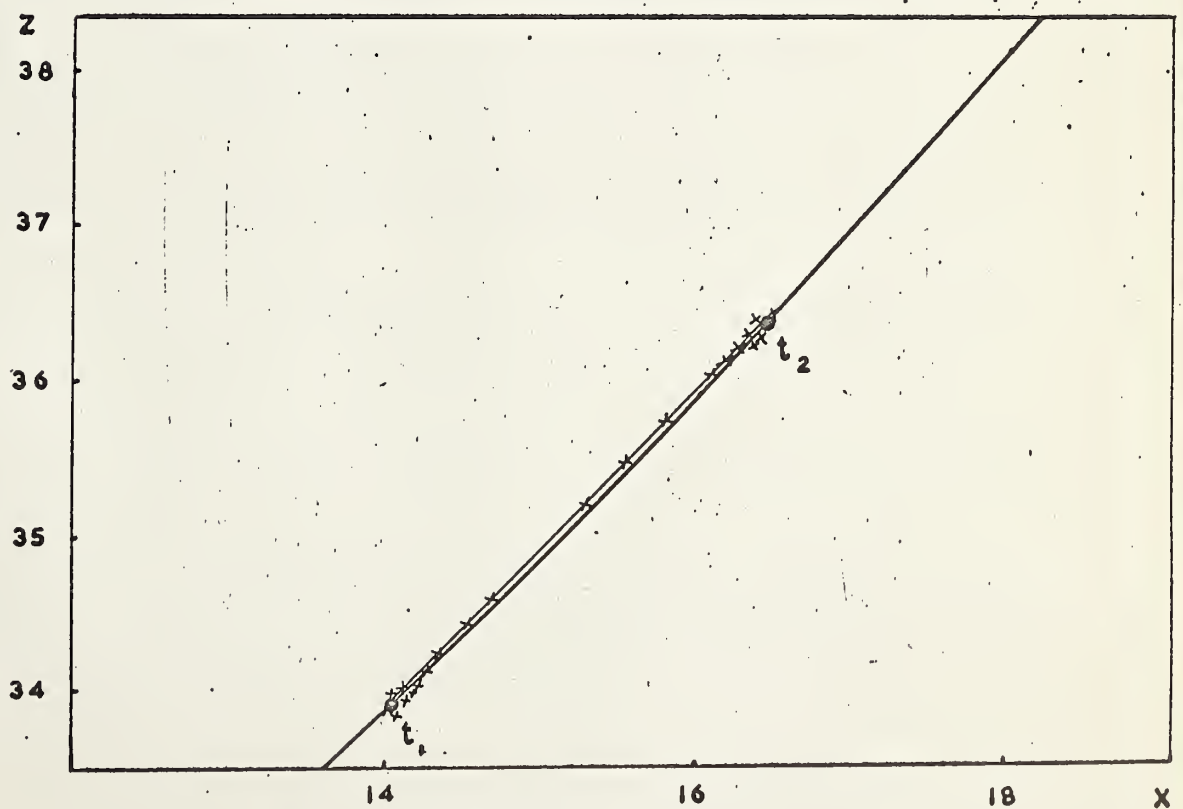


FIGURE Vb

CASE II Mixing of two ordinary leads





## BIBLIOGRAPHY

- Geiss, J. and Goldberg, E.D., 1963, *Earth Science and Meteorites*; North Holland Publishing Company.
- Kanasewich, E.R., 1962, Approximate Age of Tectonic Activity Using Anomalous Lead Isotopes; *Geophysical Journal of the Royal Astronomical Society*.
- \_\_\_\_\_, 1963, Quantitative Interpretations of Anomalous Lead Isotope Abundances; Ph.D. Thesis U.B.C.
- \_\_\_\_\_, 1966, The Interpretation of Lead Isotopes and Their Geologic Significance (Radiometric Dating for Geologists); J. Wiley & Sons, in press.
- Kanasewich, E.R. and Slawson, W.F., 1964, Precision Intercomparisons of Lead Isotope Ratios; *Geochim and Cosmochim. Acta*, Vol. 28.
- Masuda, A., 1964, Lead Isotope Composition in Volcanic Rocks in Japan; *Geochim and Cosmochim Acta*, Vol. 28.
- Russell, R.D. and Farquhar, R.M., 1960, *Lead Isotopes in Geology*; Interscience Publishers.



## CHAPTER II

## ORIGIN OF CONTINENTS

GEOLOGIC PROVINCES

The continents may be split into geological provinces on the basis of fold belts, foliations, and K-Ar, Rb-Sr chronological methods. For instance, the area we are discussing now has been divided into the Slave, Churchill and Bear Provinces. It has also been demonstrated that certain ages continually reoccur over widespread areas when K, U and Rb dating methods are used. These dates may be related to severe periods of metamorphism during which rocks and minerals recrystallized. For instance, we have already indicated that significant events occurred in the Slave Province 2470 and 1780 m.y. ago. Often the events in one area of the earth may be correlated with events in another remote area. The dates of such events have been termed the "magic numbers" of tectonophysics. An example is the problem posed by the K-Ar histograms of Slave and Superior Provinces. Since the "magic numbers" (2500 m.y., 1800 m.y.) seem to turn up for both Provinces we are beset by a problem.

- (a) Did Superior and Slave Provinces form contemporaneously as one continent and then split?
- (b) Did Superior and Slave Provinces form as one continent and not split but merely continue as one sialic plate underneath Churchill Province?
- (c) Did Slave Province form contemporaneously but separately from Superior Province?
- (d) Did Slave Province form as a small fragment later than Superior Province?

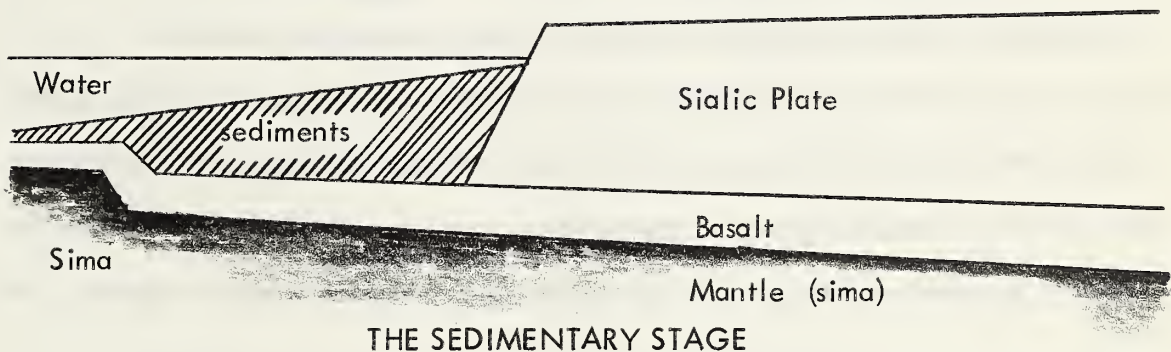
Utilizing the lead method in dating ancient events, we shall hope to shed some light on the answer to this problem.



## A THEORY DISCUSSING CONTINENTAL GROWTH\*

As postulated here, the continents have been built up as the result of a number of growth cycles. The earliest cycles, which took place in the Archean, led to the creation of the Archean segments. The youngest cycles which terminated during the Proterozoic and Phanerozoic, each may be divided into three stages, sedimentary, orogenic, and stabilization.

The Sedimentary Stage is a time during which rocks exposed on the surface of pre-existing continents were weathered and the products deposited upon the sima in an adjacent ocean basin (an ensimatic geosyncline). A certain amount of miogeosynclinal accumulation also occurred on the margins of these continents. Each sedimentary stage was terminated by the onset of orogenesis, a process which is assumed to be linked, along with continental drift, to convection in the mantle.



Each orogenic stage seems to have occurred during a period of relative movement between the continent and the adjacent ocean basin. This stage is believed to have lasted about 300 million years and to have been divided into two phases.

- (1). Fracturing in the mantle and Sima.

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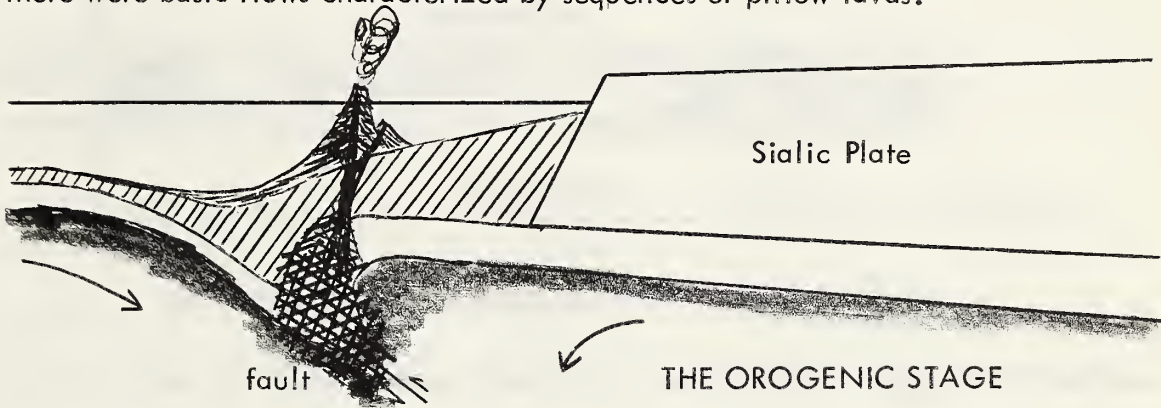
\* After H. A. K. Charlesworth (Personal Communication).





## (2). Flowage in the mantle and Sima.

The first phases saw the formation of such features as earthquake fracture systems, oceanic trenches and volcanic archipelagos. The volcanoes spewed forth vast quantities of material from below the sial. The composition of this magma was more acid than the parent sima. In many instances part of the extruded material was recycled. As the first phase drew to a close the material consisted more of Andesitic flows interbedded with volcanic tuffs - whereas during the initial part, there were basic flows characterized by sequences of pillow lavas.



A fracture system developed and relative movement along the fault produced violent earthquakes. Sediments were dragged down the fault causing a trench to develop. The generation of heat due to various processes caused melting and resulted in the formation of a volcanic archipelago. As more sediments were recycled the volcanics became more and more acidic and the geosyncline filled up.

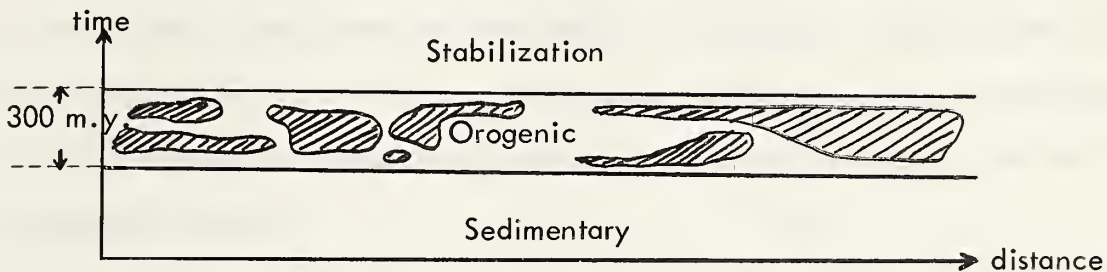
Continued crustal shortening initiated the second orogenic phase. The geosyncline was compressed and vertically extended producing deformation, metamorphism, granite emplacement and mountain building. The period of orogenesis seems to have consisted of several separate major and minor episodes. The minor episodes occurred sporadically in space and time throughout the geosyncline, while the major episodes affected the entire geosyncline. At the same time the deepening mountain roots caused metamorphism of the deeply buried roots, preferential melting of the acidic constituents, and the diapiric transfer of granitic material upwards. In the emplacement of





these granitic bodies lead mineral deposits may have been formed. At the termination of the orogenic stage all the minor phases coalesced to form one continuous primary mountain chain.

At the time when erosion removed material from the uplifted area faster than it was replenished and the period of mountain building stopped, then the stabilization stage began. It was characterized by epeirogenic uplift, normal faulting, and finally peneplanation.



### THE EXTENT OF ONE OROGENY IN TIME AND SPACE

Since the process of ore formation occurs during the orogeny this stage can be dated radiogenically. The orogeny corresponds to the time of removal of the lead from a mantle or sub-crust to a crustal environment.

### ARCHEAN SEGMENTS

Archean segments, for reasons to be discussed below, probably developed in a somewhat different manner from Proterozoic segments. The early history of an Archean segment is impossible to ascertain since no geological record of those times exists. However, the process of growth is envisaged as having begun with the local extrusion onto the sima of andesitic lavas. The problem of how and why a period of orogenesis developed locally on a crust that was uniformly oceanic over the whole surface of the Earth is a difficult one; perhaps the fractures required for the production of andesitic magma were localized by small rafts of sialic material left over from the molten stage of the mantle. In any event, the first orogenic stage which of course, was not preceded by a sedimentary stage, probably consisted of the accumulation of volcanic rocks



and sediments derived from volcanic islands, deformation of these rocks, and uplift to produce the first primary mountains. The depth of the ocean at this time had a considerable influence on the nature of the orogenic process. As previously mentioned, the post-orogenic thickness of sial was dependent both on amount of crustal shortening and on oceanic depth. Since it is reasonable to assume that the latter is increasing with time, and that the former has remained constant, the sialic thickness at the close of this first orogenic stage was smaller than that after subsequent periods of orogenesis. Since grade of metamorphism is a function of depth of burial, few high grade metamorphic rocks were produced during this first period of orogenesis, and furthermore, in the scarcity of partial melting to produce magma, few acid igneous rocks formed.

Since oceans are assumed to have been shallower during the stabilization stage of this first growth cycle than during those subsequent, the stabilization thickness of this first sialic plate was less than that of younger segments. If a sialic plate was unable to withstand subsequent tectonic compression, during the orogenic stage in the second cycle of growth, both it, and the accumulated sedimentary and volcanic rocks underwent orogenesis, obliterating evidence of the original orogeny, and leading to the creation of a single sialic plate. It is felt that the sialic plates early in the earth's history were unable to withstand later deformation, both because they were comparatively thin, and because they were made up entirely of low grade metamorphic rocks. If the oceans had deepened sufficiently by the time the second orogenic stage occurred, all the manifestations of orogenesis, including high grade metamorphism and partial melting to produce acidic magmas would have developed. In this case, the second period of orogenesis was the last to affect the Archean segments. However, it is much more likely that it took more than two periods of orogenesis to create a sialic plate thick and strong enough to withstand later deformation.

From the preceding discussion, a stabilized Archean segment could be expected to differ from younger segments in the following ways:



Points 1-4 are observations upon which the theory of continental growth is built.

(1). A greater proportion of rocks of volcanic origin than is the case with Proterozoic segments. This may result from the absence of a sedimentary stage in the first cycle of growth together with the smallness of the sialic plates from which materials were derived during subsequent Archean sedimentary stages.

(2). Few sandstones or quartzites. During Archean sedimentary stages few sandstones were laid down because acid igneous rocks were all but absent in sialic plates built during previous growth cycles.

(3). Few carbonates or their metamorphic equivalents. This may be attributed to one or more of a number of factors, some of which are as follows: (a) the small concentration in Archean seas of calcium produced during the subaerial weathering of feldspars and ferromagnesian minerals because of the smallness of the surface upon which weathering took place, (b) the scarcity of organisms required in the deposition of organic limestone, (c) the tendency for ensialic sedimentary successions of Secondary Mountains, which today carry appreciable proportions of limestone, to be progressively removed by erosion, ensimatic in origin and thus deficient in limestone, and (d) a low marine pH caused by the high  $\text{CO}_2$  content of the Archean atmosphere.

(4). A lower average grade of metamorphism than is the case with the Proterozoic segments. The ratio of "granitic" bodies formed by a more or less in situ reconstitution to those of magmatic origin should be lower in the older than in the younger segments and there should be fewer anorthosite bodies and other high pressure rock types in the Archean segments.

Although no statistical information regarding the relative proportions of volcanics, sandstones, carbonates, high-grade metamorphics and "migmatitic granites" in Archean and Proterozoic segments is available, a somewhat cursory examination of available information does tend to support the conclusions listed above.

Geological observations in Slave Province discussed in Chapter I, tend to





correspond to the various stages during the construction of a segment. These stages as they might apply to the area under discussion.

- (1). A thickness of sediment from some protocontinent was deposited in the primeval sea.
- (2). With the onset of orogeny the rocks of the Yellowknife Greenstone belt (Division A) were poured out upon the sea. Some flows were andesitic and others dacitic. All were later metamorphosed.
- (3). Tuffs interbedded with greenstones (Division B) represented a pause in the outpouring of lavas where sedimentary conditions prevailed. The lead present in these tuffs should be ordinary, representing the time of their deposition. Sedimentary conditions prevailed with the deposition of shales, argillites, greywackes and conglomerates of Division C, all later to be metamorphosed.
- (4). Extensive granite emplacement and granitization took place. It is likely that the original sediments underneath Division A were melted and granitized. At this time, of course, they were deeply buried. Magmatic differentiation processes produced granites of a more acidic nature which were injected towards the surface. The western granitic mass of the Yellowknife area shows sharp contacts in places, as well as granite dykes. The Prosperous Lake granite exhibits intrusive features, is dated as younger than the western mass, and is more acidic. Therefore, it could be a later result of the granite forming process characterizing this stage of continental growth.
- (5). The orogenic phase terminated with the injection of dykes (N 70° - 80°E swarms).
- (6). The stabilization phase was characterized by a period of intense faulting and erosion of the continent into the surrounding ocean..
- (7). A long period of sedimentation commenced prior to the construction of Bear and Churchill Provinces.





## CHAPTER III

## GEOLOGY OF THE YELLOWKNIFE AREA\*

Many of the samples used for this thesis were obtained from orebodies in the Giant, Con Rycon, Negus and Ptarmigan Mines (located near Yellowknife; see Map I) and surrounding rocks. Consequently, we are interested in the environment and origin of these orebodies. Most of the gold-quartz deposits occur in chlorite schist zones (or shear zones) cutting greenstones or in quartz lenses. These deposits represent concentrates of sulphur, arsenic, zinc, antimony, gold and silver, as well as lead. Chemical evidence indicates that the influence of a strong metamorphism caused metallic minerals in the greenstones to mobilize and accumulate in shear-zone systems (Boyle, 1961). This same process also affected the sediments.

The rocks around Yellowknife have been roughly classified according to their constituent elements and order of genesis. Extensive geological surveys have resulted in a complex picture of the mineralization involved during the history of the rocks. The oldest rocks of the Yellowknife Group are simply labelled Division A. These are a thick succession of massive and pillowed andesite and basalt flows, tuffs and agglomerates. Dome flows extend for several miles. Division A is cut by diorite and gabbro dykes and sills. Overlying Division A, and apparently conformable with it, are the rocks of Division B. These are a thick series of sediments with dacites, agglomerates and tuffs interbedded with some conglomerate and greywacke near the base.

Both divisions are metamorphosed, folded and deformed. The dykes cutting Division A have *become* meta-diorite, meta-gabbro dykes while the sediments have been transformed into slate, quartzite, argillite, and phyllite. Formerly considered as part

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\* From Boyle



of Division B, the upper layers have been classified in a new division. Intruding and altering Divisions A and B, because of their sedimentary character, are massive granite bodies with associated pegmatites, stocks and dykes. The contact is sharp in some areas, although xenoliths appear in others. Several phases of granitic material are evident with the first generally the most basic. The first phase, for instance, is often granodiorite later cut by phases containing more microcline and perthite with less hornblende. Final phases are granite stocks and dykes. The Prosperous Lake granite consists of an older granite phase and a younger granite pegmatite phase, and seems to be the youngest granite "intrusive" body. Quartz-feldspar-porphyry dykes cut the greenstones in some places, as well as the early quartz lenses, but are cut by shear zones.

Both Divisions A and B have been greatly altered by the granites and may be divided into distinct facies depending upon the degree of metamorphism. Closest to the contact is the amphibolite facies. Original features such as pillows are retained. Epidote, quartz, magnetite and ilmenite occur in small amounts with garnets in the tuff. This facies grades into the epidote-amphibolite facies. Epidote is developed with pyrite and pyrrhotite occurring as minor accessory minerals. The greenschist facies is found in the cooler zone. Sulphides are often present as accessory minerals. The rocks of Division B have been altered to quartz-mica schists and hornfels with segregations of andalusite garnet and staurolite. Unaffected by metamorphism and cutting all the rocks are diabase dykes and sills which themselves are cut and displaced by late faults. These dykes occur in four sets.\*

**Set I.	N 70° - 80° E
Set II.	N 0° - 30°E
Set IV.	N 30° - 60° W

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\* A.P. Leech, 1965.

\*\* Set III is not in the thesis area.



In addition to the dykes cutting it, Division A is also cut by shear zones and fractures in which mineralization has occurred. These are classified according to their relative ages and structures as follows:

- (1). Early pre-shear-zone fractures
- (2). Shear zones
  - (a). parallel lava flows in strike and dip
  - (b). transect lava flows
- (3). Pre-diabase fractures cutting the shear zones.

Pre-shear Zone Fractures: These occur predominantly in the greenstone rocks and enclose lenses of quartz with small grains of pyrite imbedded in places. Fractures in the dykes and massive flows are short, and appear to have been caused by tensional forces acting during early deformation of the greenstone. They have a random distribution of strike and dip.

Shear Zones: The first structural type which parallels the lava flows in strike and dip contains few minerals, but those that transect contain the most minerals, including the major economic gold deposits in the Yellowknife greenstone belt. The parallel shear zones in general cut the early meta-gabbro and meta-diorite dykes and in turn are cut by the transecting shear zones. It is probable that the parallel shear zones are the result of failure along incompetent bedding planes during the initial stages of the folding of the greenstone belt, later followed by the transecting fractures as the degree of deformation affecting the greenstone advanced.

Pre-diabase fractures cutting the Shear Zones: Most of these dip nearly perpendicular to the schistosity of the shear zones with variable strikes. They are mineralized with sulphosalts and gold, and appear to be the result of tensional forces acting during a later period of deformation.

Post-diabase faults and fractures: The major faults strike N 10° W to N 40° W and dip vertical (The Kam Pud, West Bay, Hay Duck, Walsh, Ptarmigan, Vega and Madeline





Faults). Crossover faults related to these are the Martin, Townsite, Age, Negus, Akaitcho and Duck Faults. Mineralization in these faults is not extensive.

A sequence of events discussed in this section and involving the geological history of the Yellowknife area is shown in Figure VI.

An effort has been made to assemble and correlate all the known data on Slave Province and adjacent Bear and Churchill Provinces. Such an assembly should bring us nearer our goal of attaching a date to the major events affecting the Yellowknife area, and correlating these dates with events affecting Slave Province itself, as well as events associated with the construction of the nearby Bear and Churchill Provinces. Consequently, all the G.S.C. K-Ar dates and K-Ar dates for the dykes (Leech, 1965) have been studied and classified according to the geological environment and location of the rocks sampled. (See Appendix III). The locations and G.S.C. ages have been plotted on Map I. The histogram shown indicates events at 2470 and 1780 m.y.

The histogram enables us to estimate roughly the time classification of certain geologic events in the Yellowknife area, a definite improvement over the rock stratigraphic classifications of Figure VI. Such a classification is shown in Figure VII. In later chapters the lead method will accurately date the earliest events - those for which the K-Ar method is very imprecise, especially if the argon has been driven out of the old rocks by a complicated geological history. The K-Ar dates, rather inaccurately, reflect "echoes" of orogenies at times later than the actual time the rock was formed.

It is evident from the histograms corresponding to different areas of the province, as well as different rocks, that the events affecting them were episodic in nature. That is, it appears that the province was built in stages over a time interval of perhaps three hundred million years. As well, the sequence of rocks indicates that the concept of continental growth and geologic provinces is a useful one to elaborate on.





ROCK UNITS	EVENT	COMMENT
Glacial Drift		Long Period of Erosion Still in Progress
	Faults Dykes & Sills	Some apparently occurred at same time as faults.
	Diabase dykes	Intrude and cut all other rocks
	Prosperous LK. Granite Granite and Granodiorite	
	Meta gabbro dykes & sills	
Division C.	Argillite Shale and sandy shale	Shows good bedding
Division B.	Argillite, acid flows and tuffs; argillite and clastics; arkosic quartzite; basal conglomerate;	Overlies Div. A unconform- ably near Walsh LK. but in places is continuous with Div. A. Also cut by met-dykes.
Division A.	tuffs & agglomerates Andesite basalt; pillowed flows: rhyolite bands between flows.	Cut by meta-diorite dykes and sills and probably con- temporaneous with some lava flows.

FIGURE VI

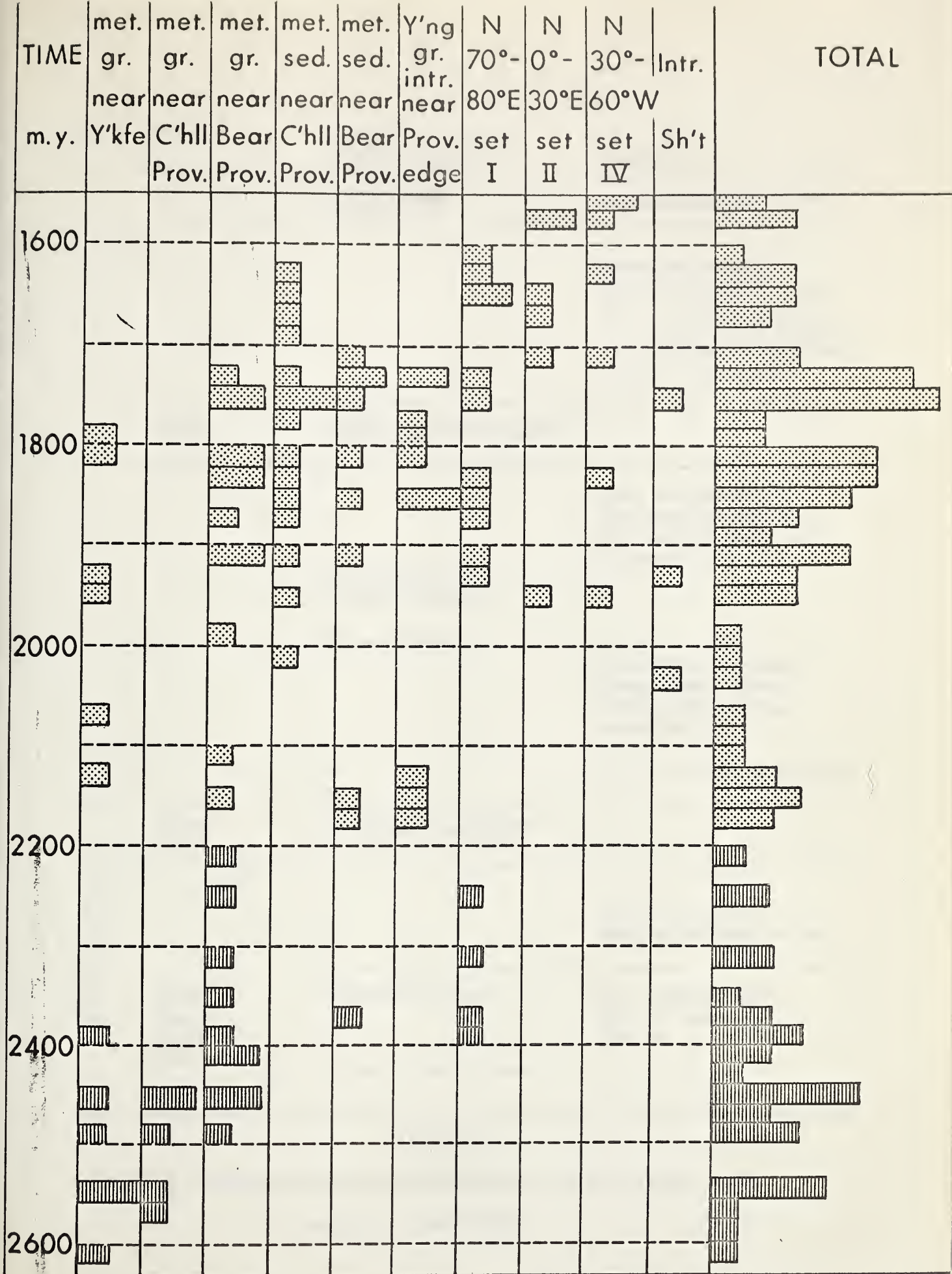
SEQUENCE OF EVENTS INVOLVING THE FORMATION OF THE YELLOWKNIFE  
AREA GAINED FROM GEOLOGIC EVIDENCE











A K'- Ar Histogram showing events



EON	TIME	TIME CLASSIFICATION	EVENTS
		Glacial Drift	Extensive Erosion
			Extensive faulting Dyke intr. with faulting Intr. N - 30° - 60° W, N - 0° - 30° E dykes Metamorphism in Slave Prov. Gran. Int. into Snare
	1780	HUDSONIAN OROGENY	
		Gt. Slave LK. Gp. (Churchill Prov.)	Start of formation of Bear and Churchill Prov. with Met. of Snare to Gt. Slave LK Groups.
		Snare (Bear Prov.)	Deposition of Sediment along edges of Slave Province during long period of Erosion.  N 70° - 80° Dyke Intrusions.
	2470	KENORAN OROGENY	
A R C H E A N	2615 from (G.S.C.) pub.	Yellowknife Group	Granite Intrusions Met. of Yellowknife Gp.  Div. C Deposited in Div. B Sequence Div. A

FIGURE VII

SEQUENCE OF EVENTS INVOLVING FORMATION OF THE YELLOWKNIFE  
AREA ON A TIME BASIS





## BIBLIOGRAPHY

- Boyle, R.W., 1961, The Geology, Geochemistry and Origin of the Gold Deposits of the Yellowknife District; G.S.C. Memoir 303.
- Henderson, J.F. and Brown, I.C., The Yellowknife Greenstone Belt; G.S.C. Paper 52-28.
- Leech, Alice Payne, 1965, Precambrian Basic Intrusive Rocks; M.Sc. Thesis, University of Alberta.
- Leech, G.B., Lowdon, J.A., Stockwell, C.H. and Wanless, R.K.; Age Determinations and Geological Studies; G.S.C. 1963, 1962, 1961, 1960, 1959.
- Marshall, R.R. and Hess, D.C., 1960, Determination of Very Small Quantities of Lead; Analytical Chemistry, Vol. 32, no. 8.
- Stockwell, 1957, Geology and Economic Minerals of Canada; G.S.C.
- Wanless, R.K., Boyle, R.W., Lowdon, J.A., 1961, Sulphur Isotope Investigation of the Gold Quartz Deposits of the Yellowknife District, G.S.C.



## CHAPTER IV

## ANALYTICAL DATA &amp; INTERPRETATION

CLASSIFICATION OF SAMPLES

In view of later results concerning their isotope ratios and their locations it was deemed advisable to divide the samples into four groups.

- Group I        Those samples of galena and pyrite obtained from the mines around Yellowknife and nearby areas. They are disseminated and impure\* samples. (See map on following pages).
- Group II        Those samples obtained far from Yellowknife but still within the confines of what is considered to be Slave Province.
- Group IIa       Those samples on the boundary. Slave and Churchill Provinces.
- Group III       Those samples on the South shore of Great Slave Lake which consist mostly of clean cubical galena. (All in Churchill Province).
- Group IV        Galena samples from Pine Point.

The location of each sample and its description is shown in the accompanying map and table.

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\* Present with large amounts of whole rock and various sulphides.



A TABLE DESCRIBING THE SAMPLES

SAMPLE NAME	GROUP I
	DESCRIPTION
Ptarmigan	Traces of galena in Pyrite and Chalcopyrite
Discovery (Py)	Pyrite and Pyrrhotite in chloritized zone and quartz vein.
Discovery (Pb)	Galena found in same mine.
Tom Pit	Traces of galena in massive quartz vein in Yellowknife Group
Walsh LK	Some galena associated with sphalerite (Upper Y.G.)
Crestaurum	Small specks of pyrite and galena in quartz vein.
Likely LK	Massive galena in Yellowknife Group.
Indian Mtn. Mine	Massive disseminated galena in chloritized zone. (63° 09', 110° 50')
	GROUP II
Cameron River	In volcanics of Yellowknife Group - very impure disseminated galena in traces throughout a sulphide mass (Py, Chpy)
Duck Lake	Galena in mineralized fault zone.
Rae	Disseminated galena and sphalerite in quartz vein (associated with Cu as well.)
Post Island	Galena
	GROUP IIa
Basille Bay	Galena from small fracture in chloritized Rocks of Wilson Island Group (62° 10' ; 111° 22')
Norris LK	Massive Galena associated with Chalcopyrite, Pyrite and Quartz (64° 25' ; 115° 45')
Windy Point	Pure galena cubes (61° 18'; 109° 50')

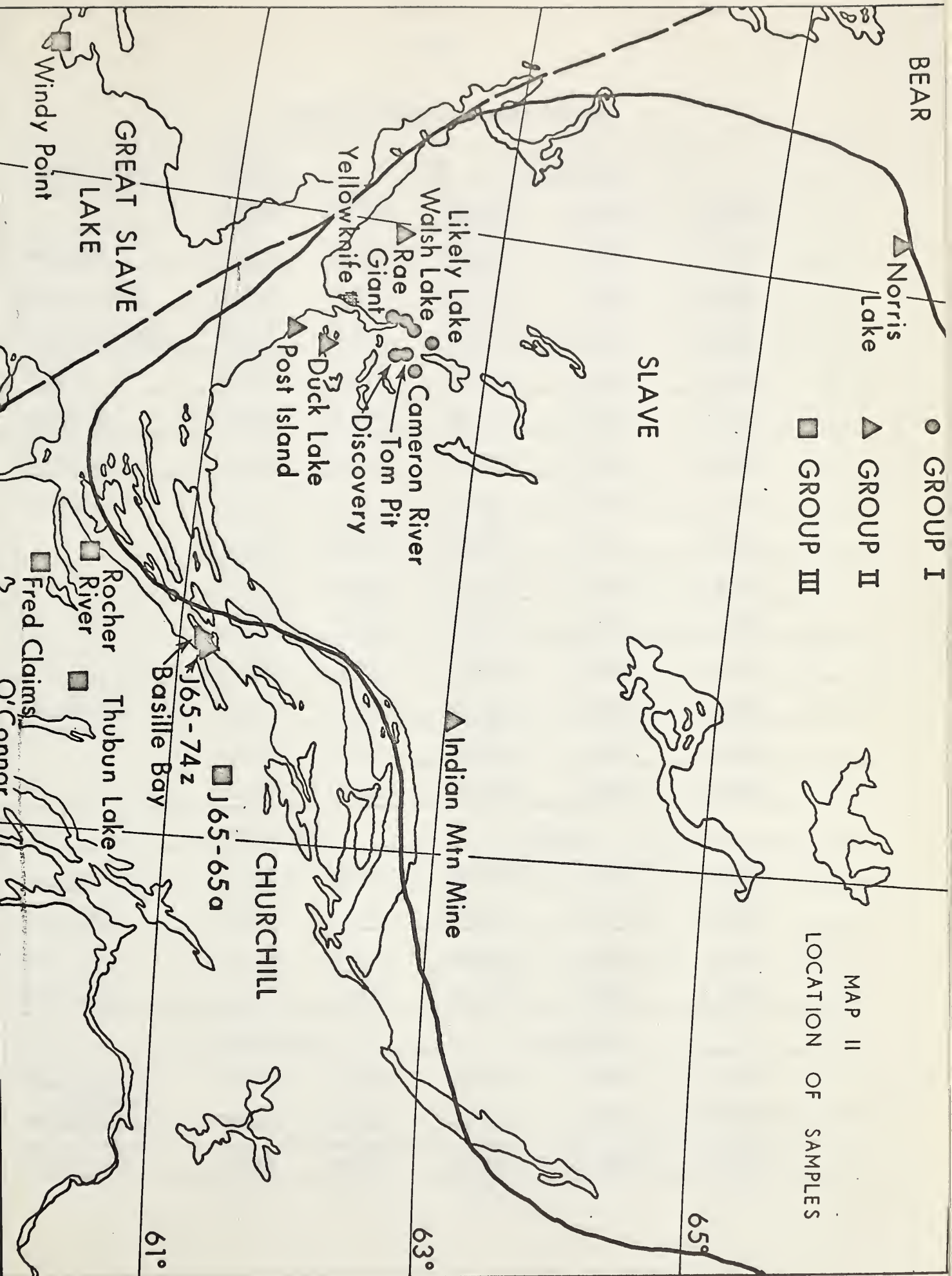


SAMPLE NAME	GROUP III
	DESCRIPTION
Rocher River (z-144)	Massive galena (61° 42', 112° 09')
Thubun Lake (z-124)	Galena
Fred Claims	Galena in quartz vein (61° 28'; 112° 00')
French Lake (PR-3-14)	Galena
O'Conner LK. (z-197)	Galena in quartz vein. (61° 18'; 111° 04')
J-65-65-a	Galena in Barite vein. Vein is fracture filling in a small fault cutting Sossan formation (62° 10.5'; 110° 23')
Galena Point	Massive galena from near Bathurst Inlet (67° 45'; 109° 50')
	GROUP IV
6009 a	Large cubes - pure galena from Pine Point
6009 b	Disseminated galena from same sample (collected by R.E. Folinsbee, 1965)
Pine Point #4	
#7	Galena all from the same general area (collected 1911)
#8	
#9	
#10	Galena from "C" locality (P-31 deposit) Almost pure galena in large cubes.
Pine Point #11	Galena some distance from mine (60° 53'; 114 ° 20')

The ratios are tabulated on the next page. The most recent ones, and the most precise, are marked with an asterisk. All are within 0.2%.









A TABLE LISTING THE LEAD RATIOS

SAMPLE NAME	GROUP I				
	(Yellowknife)				
	206/204	207/204	208/204	207/206	208/206
Ptarmigan	13.726	14.818	33.858	1.0795	2.4667
Discovery (Py)	13.739	14.831	33.396	1.0795	2.4700
*Discovery (PbS)	13.833	14.842	33.850	1.0729	2.4470
*Tom Pit	13.928	14.990	34.099	1.0762	2.4482
*Walsh LK	13.845	14.870	33.440	1.0740	2.4153
Crestaurum	14.043	15.074	34.166	1.0734	2.4329
*Likely LK	14.217	15.251	34.356	1.0727	2.4165
	14.240	15.251	34.651	1.0710	2.4334
	14.231	15.266	34.498	1.0727	2.4241
	14.253	15.284	34.362	1.0723	2.4109
	14.235	15.263	34.467	1.0722	2.4212
*Indian Mtn. Mine	14.212	15.158	33.922	1.0665	2.3868
	14.211	15.162	33.954	1.0669	2.3893
	14.212	15.160	33.938	1.0667	2.3880
GROUP II					(Slave)
Cameron River	14.198	14.960	33.975?	1.0537	2.3929
Duck Lake	15.763	15.428	35.354	0.9787	2.2428
Rae	17.134	15.957	36.898	0.9313	2.1535
Post Island	16.255	15.573	36.414	0.9580	2.2401
GROUP IIa					(Boundary)
*Basille Bay (J-65-74-a)	15.643	15.380	35.401	0.9832	2.2631
*Windy Point	19.532	16.252	38.517	0.8321	1.9720
*Norris Lake	15.650	15.375	35.330	0.9824	2.2575





GROUP III			(Churchill)		
Rocher River	16.391	15.619	36.351	0.9529	2.2177
*Thunbun Lake	15.133	15.325	34.842	1.0091	2.3024
*Fred Claims	16.172	15.540	36.170	0.9609	2.2365
French Lake	15.992	15.457	35.767	0.9665	2.2365
	16.018	15.511			
O'Connor Lake	15.990	15.511	35.913	0.9750	2.2459
*J-65-65-a	16.300	15.590	36.350	0.9564	2.2300
Galena Point	19.812	16.267	38.878	0.8211	1.9623
GROUP IV			(Pine Point)		
6009a	18.282	15.768	38.563		
	18.309	15.773	38.701		
6009b	18.299	15.768	38.672		
Pine Point #4	18.312	15.797	not run		
Pine Point #7	18.334	15.801	not run		
Pine Point #8	18.357	15.840	38.713		
Pine Point #9	18.300	15.785	38.684		
Pine Point #10	18.249	15.752			
Pine Point #11	18.291	15.756	38.379		
TORONTO ANALYSIS (Unpublished Data by permission of Farquhar).					
141 Negus	14.075	15.083	34.272	1.0716	2.4350
194 Negus	14.053	15.091	34.219	1.0738	2.4347
443 Negus	13.964	14.982	34.091	1.0729	2.4413
444 Con	13.987	14.979	34.102	1.0709	2.4381
446 Con	13.958	15.003	34.099	1.0748	2.4429
447 Giant	14.031	15.046	34.238	1.0723	2.4401
449 Ptarmigan	13.758	14.856	33.971	1.0798	2.4691
451 Dome	13.854	14.872	33.915	1.0734	2.4480





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144 Horseshoe Lake	14.051	15.036	34.211	1.0701	2.4347
1003B Broken Hill	16.116	15.542	36.068	0.9644	2.2380

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\* These are the latest analyses (Oct. 15-31) and are the most precise. (0.1%)

Many of the samples were run two or more times. In such cases the individual ratios are tabulated as well as their averages. Of course, all these ratios have been corrected to the standard and have allowed for instrument drift and the like. The values obtained for several runs of the standard are also shown on the next page in order to give an idea of reproducibility and the difference between our Lab. using a solid and the one at U.B.C. using a gas source.

The runs September 1 - 22 were made in 1964. At this time charts were read by eye, the baseline was doubtful and the sample emission was poor. Fractionation caused the ratios to be too high since emission could only be obtained for high filament currents where the sample decayed off rapidly. Reproducibility was poor. The runs April 1 to 18th, 1965 are better. A digital voltmeter\* had been installed which read the peak heights and baselines accurate to five figures (see later pages). Improved chemical procedure gave improved emission. Runs of May 17th to 19th were even better. Pine Point samples were run at this time. The last samples were run October 15th to 19th, 1965. Reproducibility was now within 0.2%.

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\* McCullough H. and Krouse, H.R., "Application of Digital Recording to Simultaneous Collection in Mass Spectrometry."



A TABLE SHOWING HOW THE STANDARD VARIED WITH TIME

Date	206/204	207/204	208/204	Quality*
Sept. 1 (1964)	16.217	15.723	36.775	(g)
6	16.314	15.804	36.919	(p)
11	16.362	15.868	37.227	(f)
15	16.313	15.811	37.064	(g)
22	16.366	15.827	37.487	(g)
AVERAGE	16.338	15.828	37.143	
Date				
Apr. 1	16.160	15.564		(f)
4	16.148	15.606	36.513	(p)
5	16.210	15.719	36.636	(g)
7	16.138	15.602	36.393	(g)
10	16.095	15.563	36.185	(g)
18	16.132	15.572	36.555	(g)
AVERAGE	16.147	15.604	36.456	
Date				
May 17 (1965)	16.140	15.571	36.233	(g)
19	16.160	15.583		(g)
Oct. 15 (1965)	16.211	15.696	36.566	(g)
19	16.221	15.704		(g)
AVERAGE	16.216	15.700	36.566	
Oct. 23	16.203	15.655	36.353	(g)
UBC Value	16.116	15.542	36.068	

\* Quality of record as far as evenness of emission, tailing and peak shape were concerned. Precision for runs before April 1965 was poor.



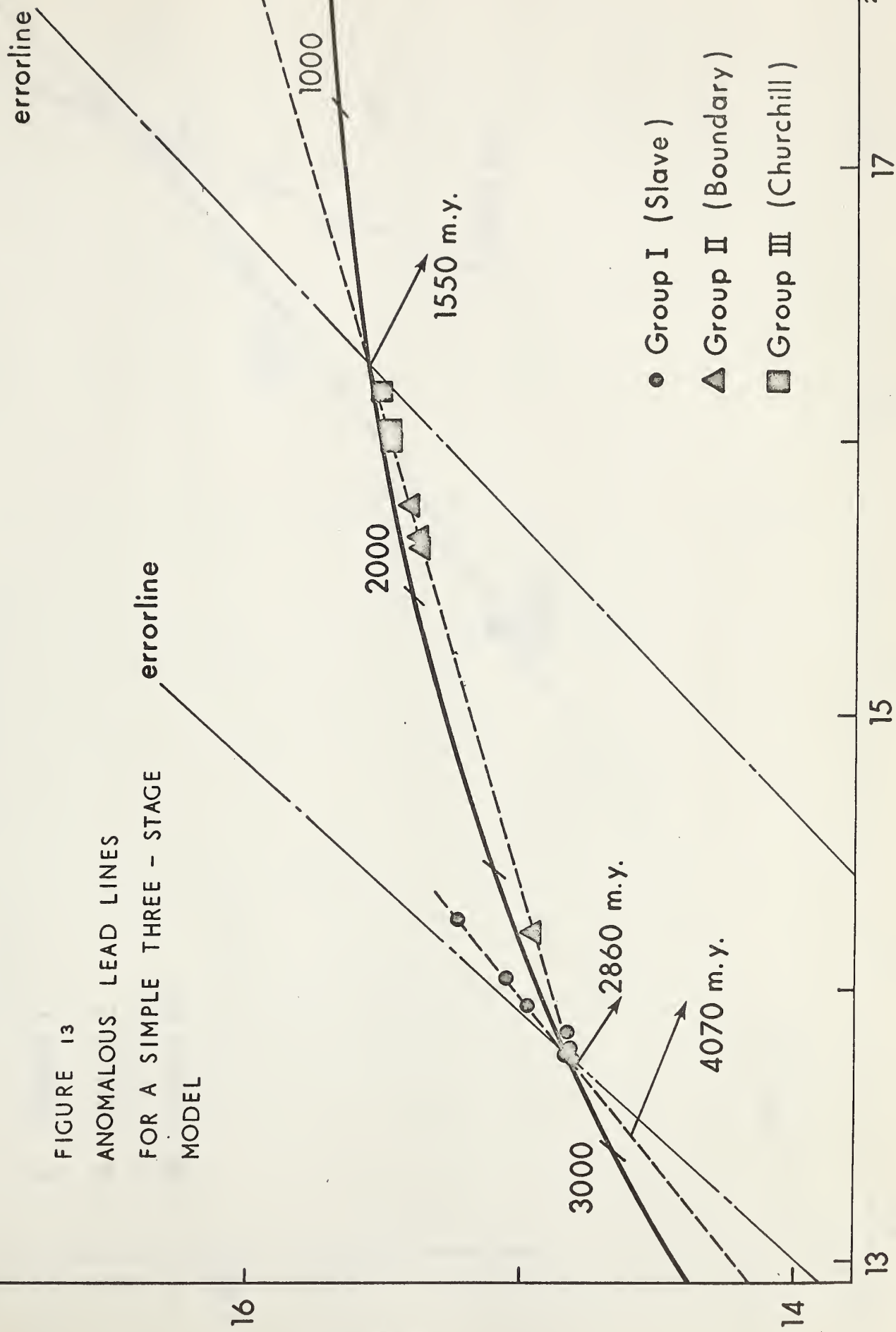
If all the ratios are plotted, one readily observes that about nine tenths of the points fall on two very well-defined anomalous lead lines. These lead lines intersect the growth curve at 4070, 2860 and 1550 million years, respectively. (FIGURE 13) The ratios from Yellowknife fall on the 4070-2860 million year lead line while those from the edges of Slave Province farther from Yellowknife and those in Churchill Province fall on the 2860-1550 million year lead line. It is noted that the ratios in Slave Province are quite anomalous and fall above the growth curve. The ratios from Churchill Province fall on the lead line but only below the growth curve. We may conclude, therefore, that some of the leads in Slave Province grew in a crustal or sub-crustal environment with variable values of  $V$  and  $W$  between the times 2860 and 1550 million years. (refer to Ch. III; Case I (Slave), Case II (Churchill)). In a major event 1550 million years ago, the leads in Slave Province were remobilized and removed from their radioactive parents. At the same time, lead was removed from the mantle and mixed with the remobilized anomalous crustal lead. Most of this ordinary lead mineralized in the Churchill Province but in both Slave and Churchill Provinces, it was mixed with the anomalous crustal lead. Both the  $y$  vs  $x$  (Fig. 13) and  $z$  vs  $x$  (Fig. 15) plots show a similar history. The  $z/x$  vs  $y/x$  (Fig. 14) plot indicates a very well-defined lead line intersecting the curve at 2860 and 4070 million years. On the basis of this data we may form a simple model.

- (1) The Earth cooled from a molten state and solidified from the inside out while still retaining a metallic liquid core. As the mantle solidified, it differentiated, concentrating Uranium and Thorium toward the surface. The concentration of U, Th probably followed an exponential function of depth, the integral of this function being equal to the total amount of U, Th in the mantle as deduced from the average amount found in stony meteorites.



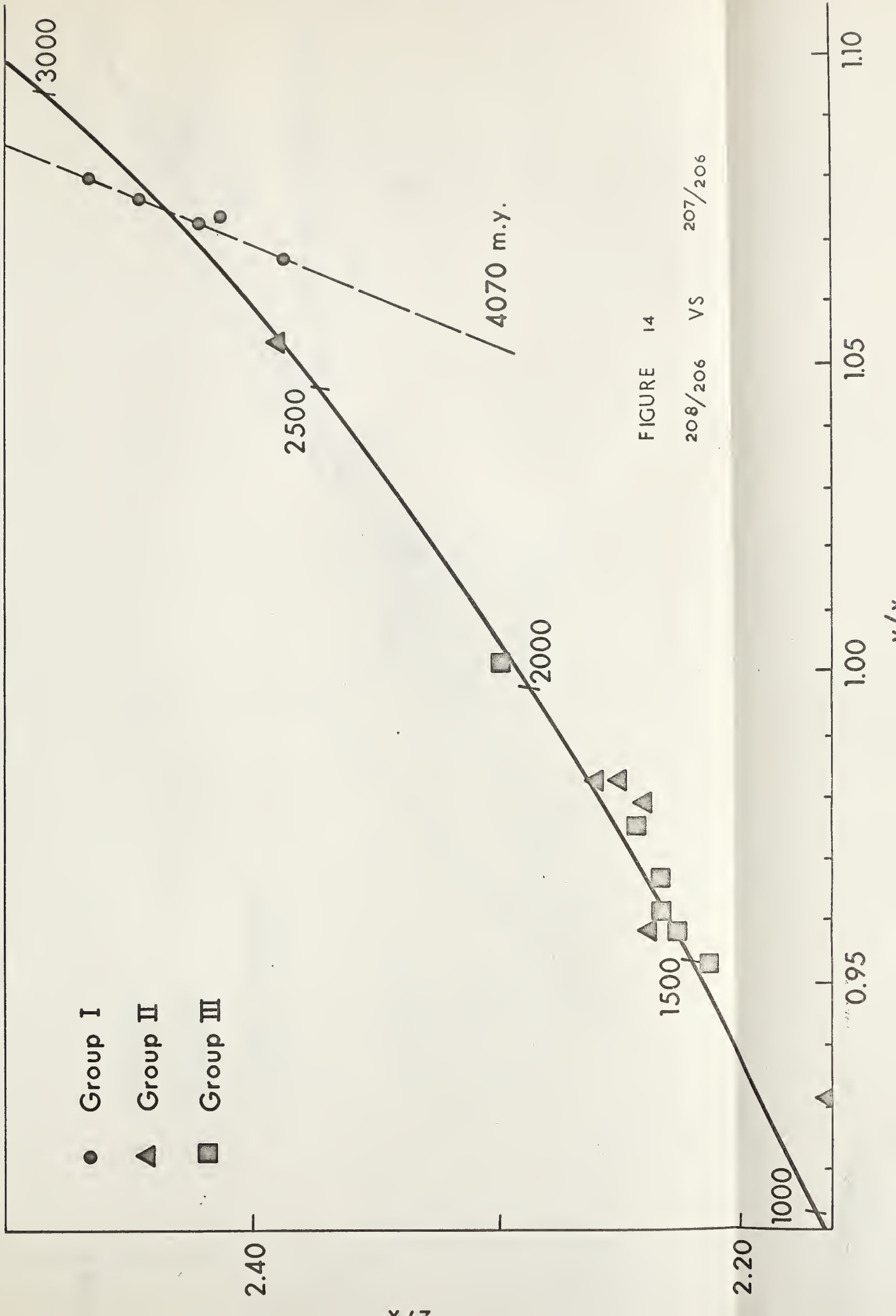


FIGURE 13  
ANOMALOUS LEAD LINES  
FOR A SIMPLE THREE - STAGE  
MODEL











● Group I

▲ Group II

■ Group III

○ Toronto Analyses

Lead from differentiated  
source

1500

1000

2000

1550 m.y.

2500

3000

2860 m.y.

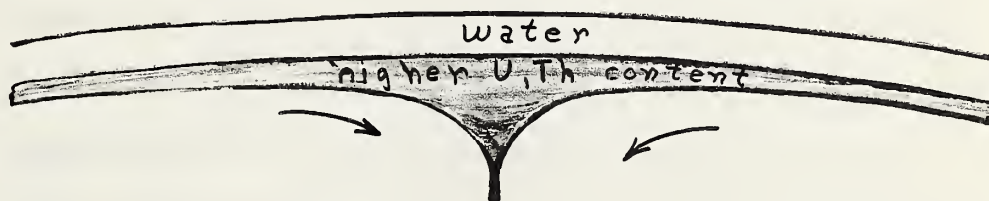
FIGURE 15

A PLOT OF  $^{208}\text{Pb}/^{204}\text{Pb}$  VS  
 $^{206}\text{Pb}/^{204}\text{Pb}$  SHOWING  
ANOMALOUS LEAD LINES

x



- (2) When all the mantle had solidified, the upper part had Lead, Uranium and Thorium concentrations corresponding to  $a_o, b_o, c_o, V_o, W_o$ . The ordinary growth curve started at this time about 4.55 billion years ago.
- (3) The solid mantle was very hot so long ago so that convection currents were much more powerful than they are now. The core may also have been smaller so that the convection cells were larger than at present. These large, powerful convection currents dragged along the uppermost layer of the mantle and accumulated it at the point where they began their descent into the interior.

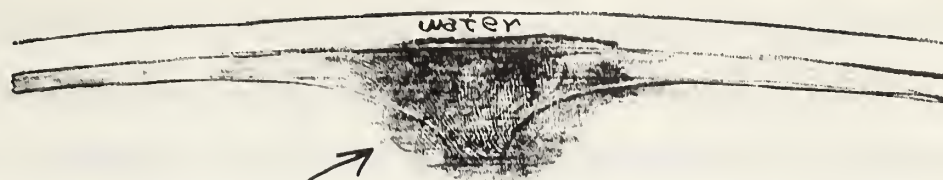


#### CONVECTION CURRENTS AS A MECHANISM FOR MAKING THE MANTLE INHOMOGENEOUS (A SPECULATION)

The resultant uneven distribution caused uneven heating and consequently partial melting in a limited area. THIS AREA BECAME THE NUCLEOUS FOR THE FUTURE FORMATION OF CONTINENTS. Partial melting further differentiated and concentrated Uranium and Thorium. The concentration was greater than that for the rest of the upper mantle which still had the parameters of the ordinary growth curve. The lead in the differentiate started to follow a set of growth curves, most of them above the mantle curve and near an average  $V, W$  for the whole differentiated magma.







Partial Melting and Differentiated Magma (richer in U, Th)

#### A MEANS OF PRODUCING ENRICHED MAGMA

- (4) From a time 4070 million years ago until a time before 2860 million years ago the lead in the differentiate grew along its growth curves. Then more than 2860 million years ago lava was poured out upon the ocean floor in massive flows (Div. A.) As the magma chamber depleted itself, the U, Th were further differentiated in the more acidic volcanics of Divisions B and C. The first phase of continent formation was completed.
- (5) Some of the lead now proceeded along another set of growth curves corresponding to new V, W values in its crustal environment. The second stage of continent formation began. Massive bodies of granite were emplaced. (The last was perhaps the Prosperous Lake Granite). Emplacement of the granites first fractured and deformed the rocks of Divisions A, B and C, then thermally metamorphosed them. During the accompanying metamorphism some crustal leads were finally mineralized free of Uranium and Thorium. This time was 2860 million years ago. If the crustal leads resided and grew radio-genically in the lava flows between the time they covered the ocean floor and the time they were mineralized they should fall on a short-period lead line. In the data no short-period lead line is obvious. If it does exist it is tangent or nearly tangent to the growth curve.



One must conclude, therefore, that the time between the deposition of the greenstones and the intrusion of the granites was short. Consequently it is difficult to say whether the lead was sweated out of the greenstones and concentrated in the fractures by thermal metamorphism associated with the granites, or whether it came from the granites themselves. In view of the discussion of Chapter IV, I would prefer to say that most of the lead came from the granites at the time the granites were emplaced perhaps 2860 million years ago. The lead in the greenstones which had originated from the enriched magma was concentrated in the fractures mixing with ordinary lead from the mantle which was associated with the granites. Then the leads not mineralized in the fractures but associated with U, Th began growing along a new set of growth curves in a crustal environment.

- (6) The third stage of continental growth began when the stabilization of the new continent caused faulting to occur. Large amounts of sediment were eroded and deposited in an ensialic or an ensimatic geosyncline around the edges of the new continent.
- (7) A new phase of continent formation commenced with the metamorphism of these sediments and the injection of magmatic material containing ordinary lead. The ordinary lead mixed with that in Slave Province and all the lead was mineralized free of Uranium and Thorium 1550 million years ago. The event was of such magnitude that most of Slave Province was remelted and metamorphosed. For this reason, the K-Ar dates have considerable scatter.

We must now discuss the few points which do not fall on the anomalous lead lines and are so far from them that the difference cannot be explained by even the most gross experimental error. These points are Thubun Lake, Rae, Windy Point,



and Indian Mountain Mine. Most are far from Yellowknife and were affected by events 1550 million years ago. To explain such anomalies a differentiated growth curve was constructed with a  $\mu$  of 9.75 (vs 8.99 for the mantle) and a  $t_1$  of 4,070 million years. This is the growth curve for the differentiated magma formed 4070 million years ago. Note that most of the isotope ratios from around Yellowknife cluster around a point on the 4070 - 2850 million year lead line corresponding to a  $\mu$  of 9.75. (See Fig. 16, 17).

We may make an amendment to our "simple" model discussed previously. Many of the leads in the Yellowknife Group came from this enriched magma of average  $\mu = 9.75$ , although some also came from the mantle. Deposited in a sub-crustal environment 2860 million years ago, they started growing along their separate growth curves. Most started from an average homogenized ratio falling on the ordinary growth curve for  $\mu = 8.99$ . The ones originating from the enriched magma however, started growing from a homogenized average ratio corresponding to a growth curve with  $\mu = 9.75$  and  $t_1 = 4070$  million years. (SEE FIG. 16). At the time of mineralization 1550 million years ago, these leads fell on two different lead lines depending on where they started. These were A-B and C-D and the ratios fell at positions where the unshaded points are located (SEE FIG. 17). Then the mixing of all these leads with ordinary lead 1550 million years ago caused them to migrate to their present observed values. Such a model will produce a distorted lead line tending to pull ratios below the ordinary growth curve up and those above down. The ratios in question all fall on such lead lines as drawn in Figure 17. Windy Point which is neither in Churchill nor Slave Province falls in such a position that mixture with Pine Point lead is indicated.

It was decided on a point of curiosity to examine the sulphur isotope ratios of the samples. These are tabulated below.







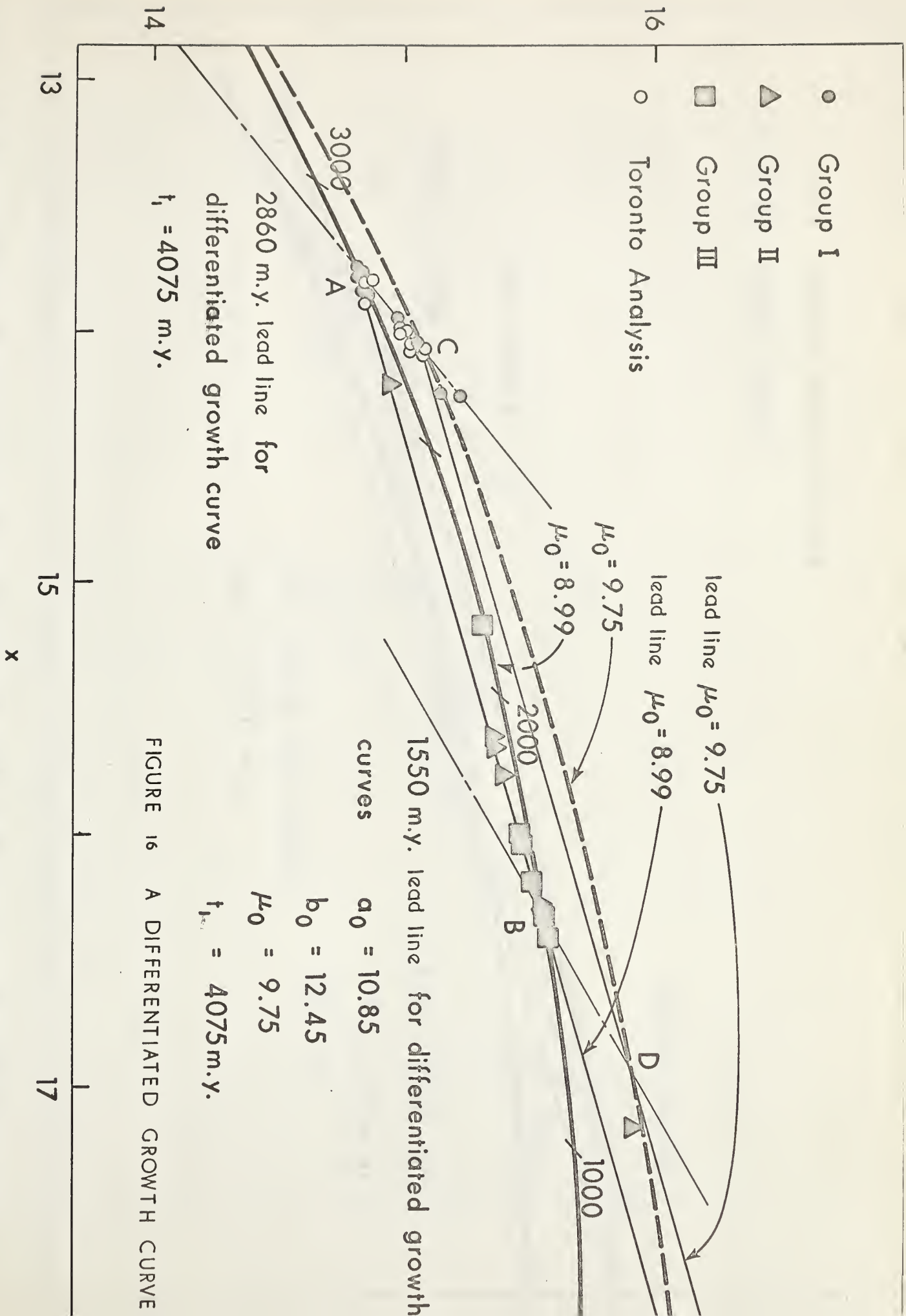


FIGURE 16 A DIFFERENTIATED GROWTH CURVE



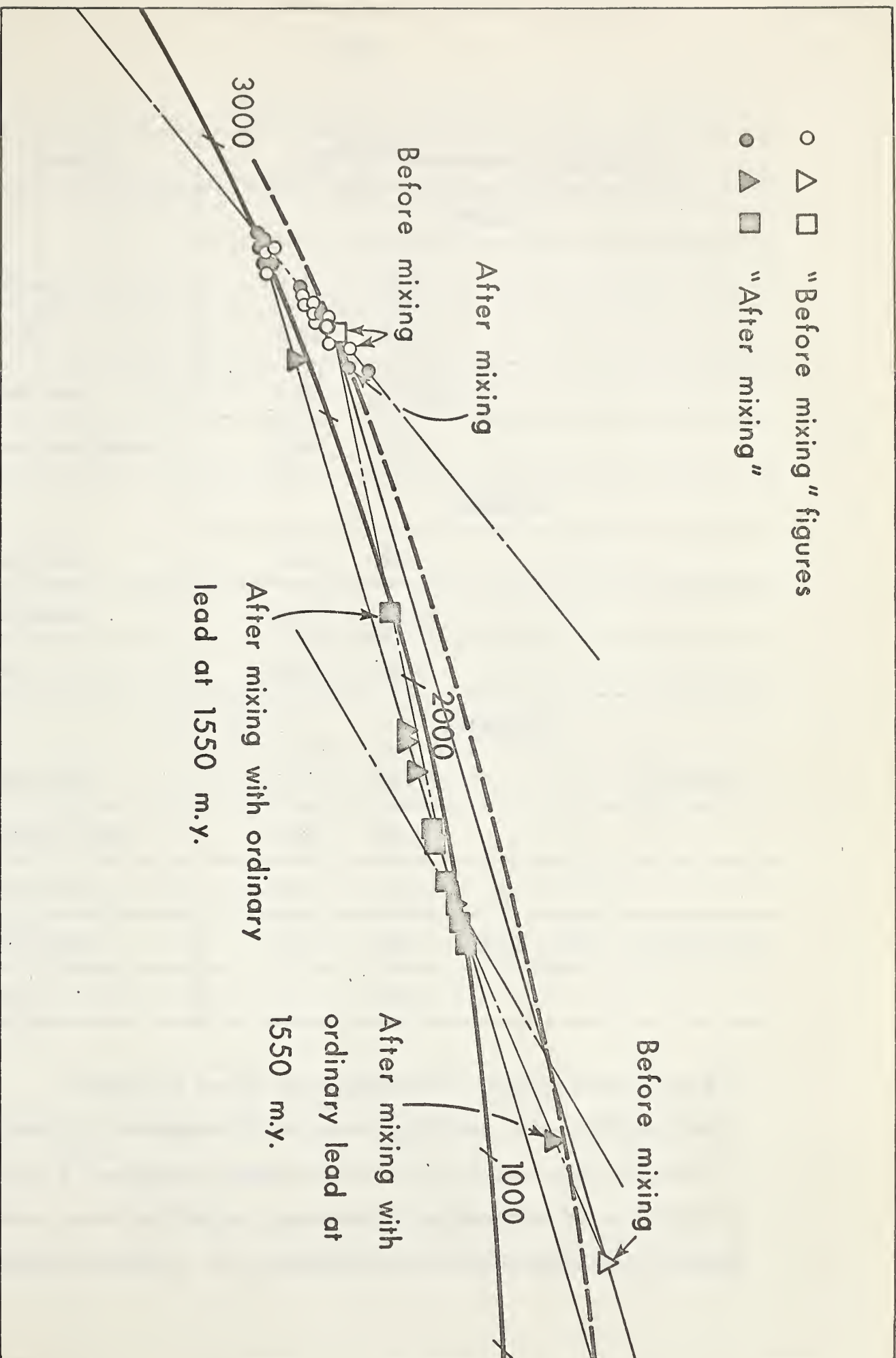


FIG 17 A possible explanation for ratios far off the simple model isochrons



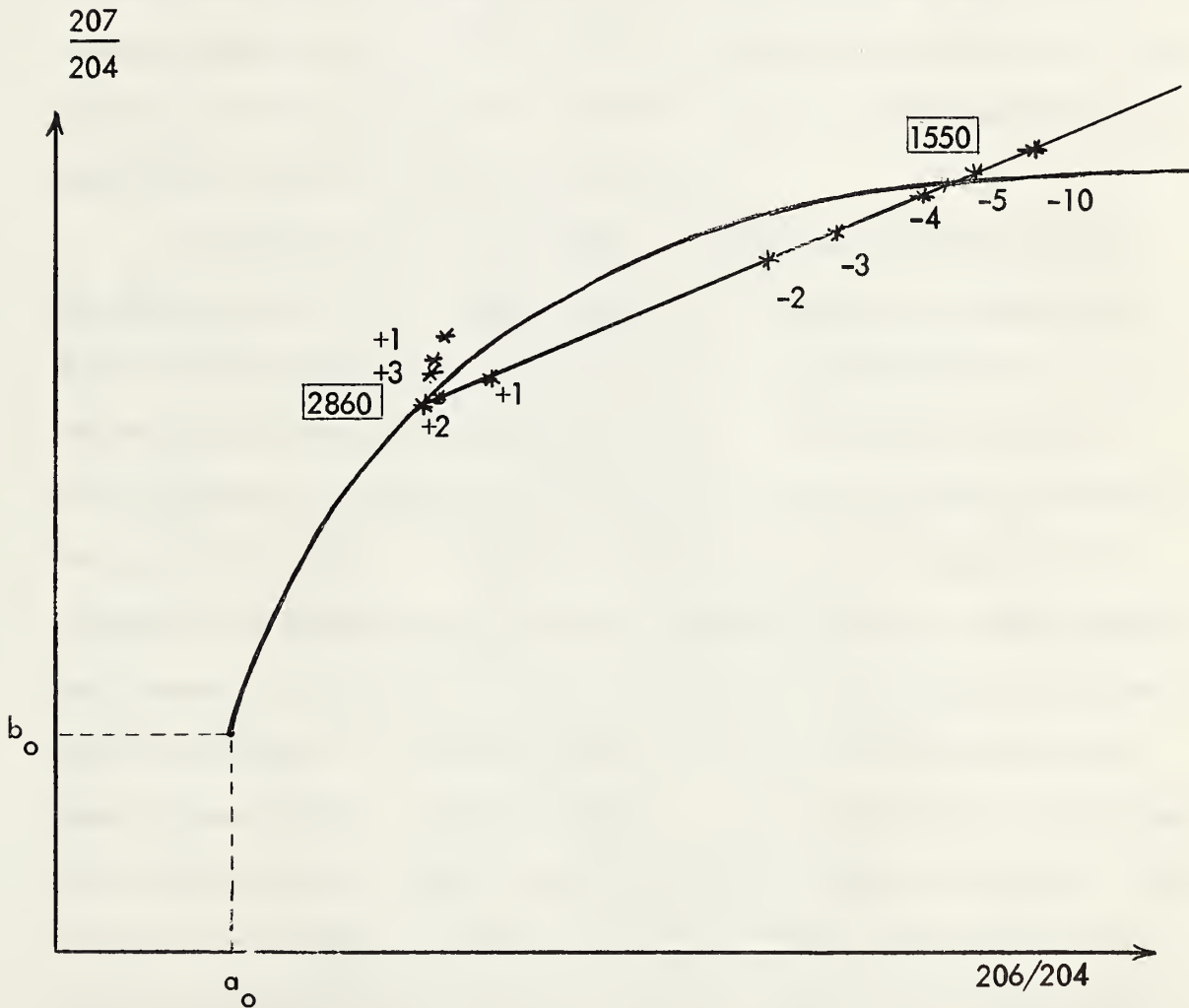
SAMPLE	$(S^{32}/S^{34})$ Enrichment (ln del ( $\delta$ ) units)		
	GROUP I		
Discovery	- 0.44	(Py.)	
Tom Pit	- 0.10	(Py.)	
Walsh Lake	1.19	(Gn. Sp.)	
Indian Mtn. Mine	2.04	(Gn.)	
	GROUP II		
Basille Bay	0.65	(Gn.)	
Post Island	- 1.73	(Gn.)	
Rae	- 5.59	(Sp.)	
	GROUP III		
Thubun Lake	1.62	(Sp. Gn.)	- 0.24 (Gn.)
O'Connor Lake	- 4.03	(Gn.)	
Rocher River	- 5.07	(Gn.)	
French Lake	- 13.2	(Gn.)	- 8.93 (Py.) - 6.55? (Sp.)
Pine Point #11	- 7.71	(Gn.)	

Inspection of the  $\delta$  values indicates that those from Group III are  $S^{32}$  enriched to a considerable degree (except significantly, those of Thubun Lake). Such an  $S^{32}$  enrichment suggests mobilization and migration of the lead over a distance under the influence of metamorphism and mineralization according to the paragenetic sequence. This interpretation fits the model characteristic of mixing





between two different leads. Thubun Lake is more enriched in  $S^{34}$  indicating a different origin or a different history. This origin may have been the differentiated magma discussed previously. Indian Mountain Mine is also  $S^{34}$  enriched. In general, it is seen that the closer the ratio lies to the 2860 million year point on the lead line the more enriched it is in  $S^{34}$  and the closer it is to the meteoritic value. This suggests that mixing between a primeval sulphide mineralizing 2860 million years ago and another  $S^{32}$  enriched sulphide forming 1550 million years ago has occurred.



DEL VALUES ON THE LEAD LINE

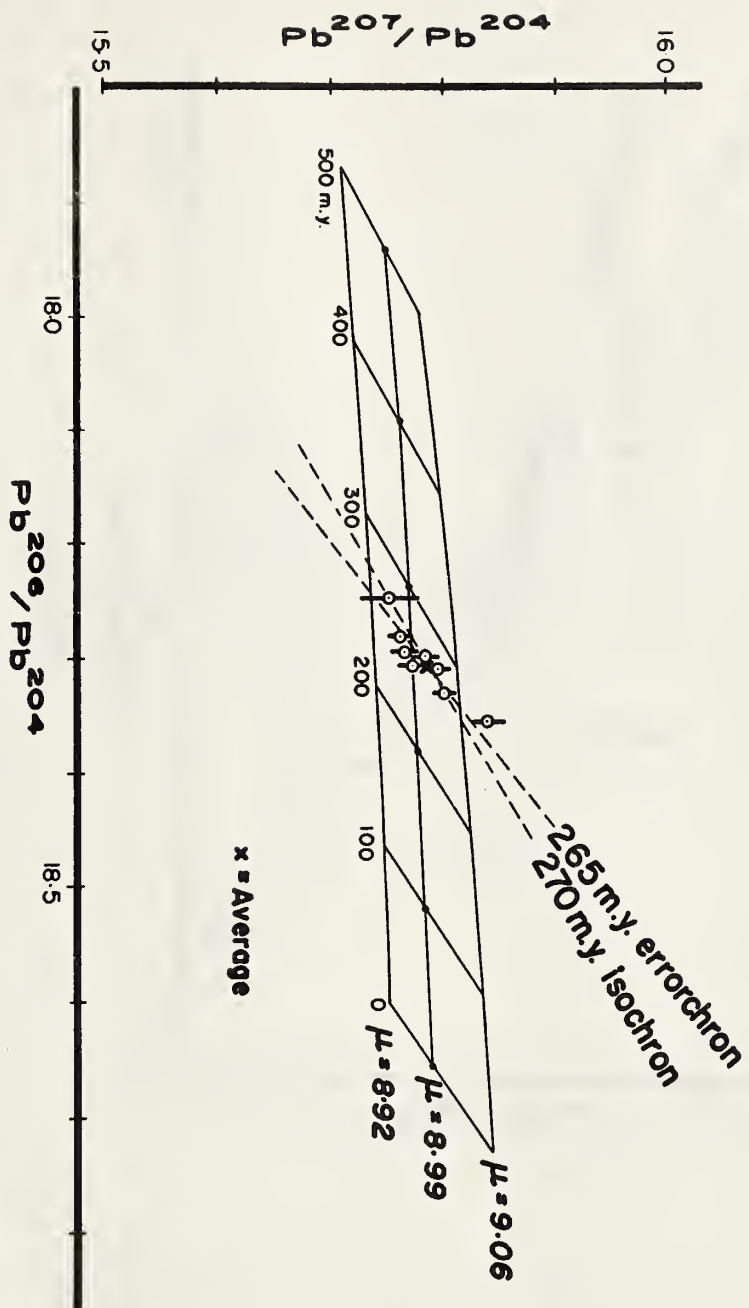


## ORIGIN OF THE PINE POINT DEPOSITS

All the lead samples determined thus far for the Pine Point area are ordinary, (See Figures) and are dated at 270 million years. This date corresponds to the Permian a period one hundred million years later than the Middle Devonian during which the Pine Point Reefs formed. One concludes therefore, that the lead did not come from the reefs, rocks or seawater of the Devonian. It was established in the reefs one hundred million years after their formation. The vast quantities of lead present at Pine Point and the fact that all the ratios measured so far are the same, indicates it came directly from a homogeneous source, the mantle. The proximity of two large intersecting faults conveniently provides a means of conveyance for the lead from the interior to the surface.

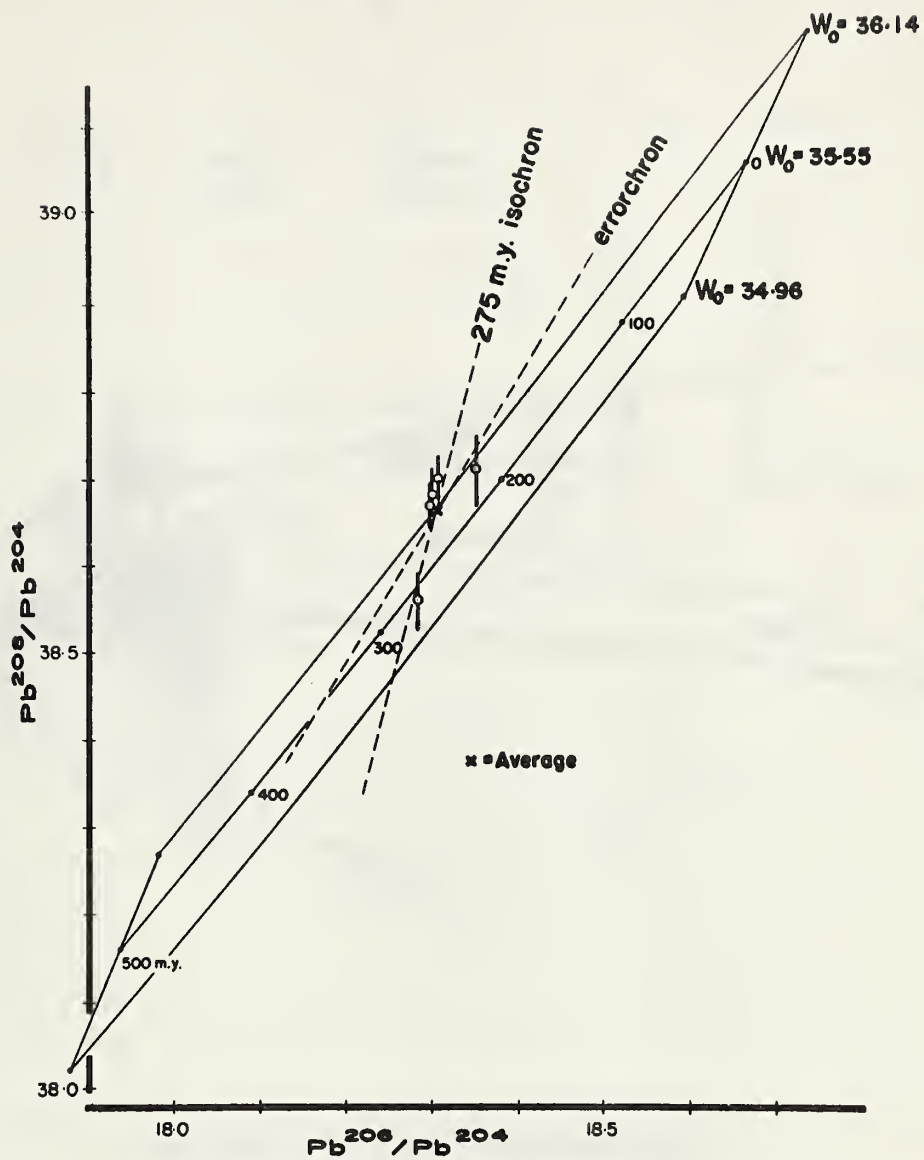
The abrupt change in environment and temperature could have caused the lead to precipitate with oceanic sulphur to form galena or else replace the Calcium in the reef to form  $PbCO_3$ , then somehow produce  $PbS$  later on. At the same time Mg may have dolomitized the reef. In any case lead from the mantle apparently combined with sulphur from the surface environment with little mixing or contamination. A degree of migration occurred as witnessed by the isotope ratio of Windy Point on the opposite side of the lake in a similar geologic environment. Windy Point falls between the 2860 - 1550 million year lead line & the Pine Point leads. It was possibly affected by some event 270 million years ago. An event 270 m.y. ago did indeed occur. Huge outpourings of lava covered the central part of B.C. and the states of Washington, Oregon and Nevada. These outpourings were the first response of the Earth to a major upheaval which would eventually produce the primary Rocky Mountains. Stage I in the renewed growth of the continent had begun.



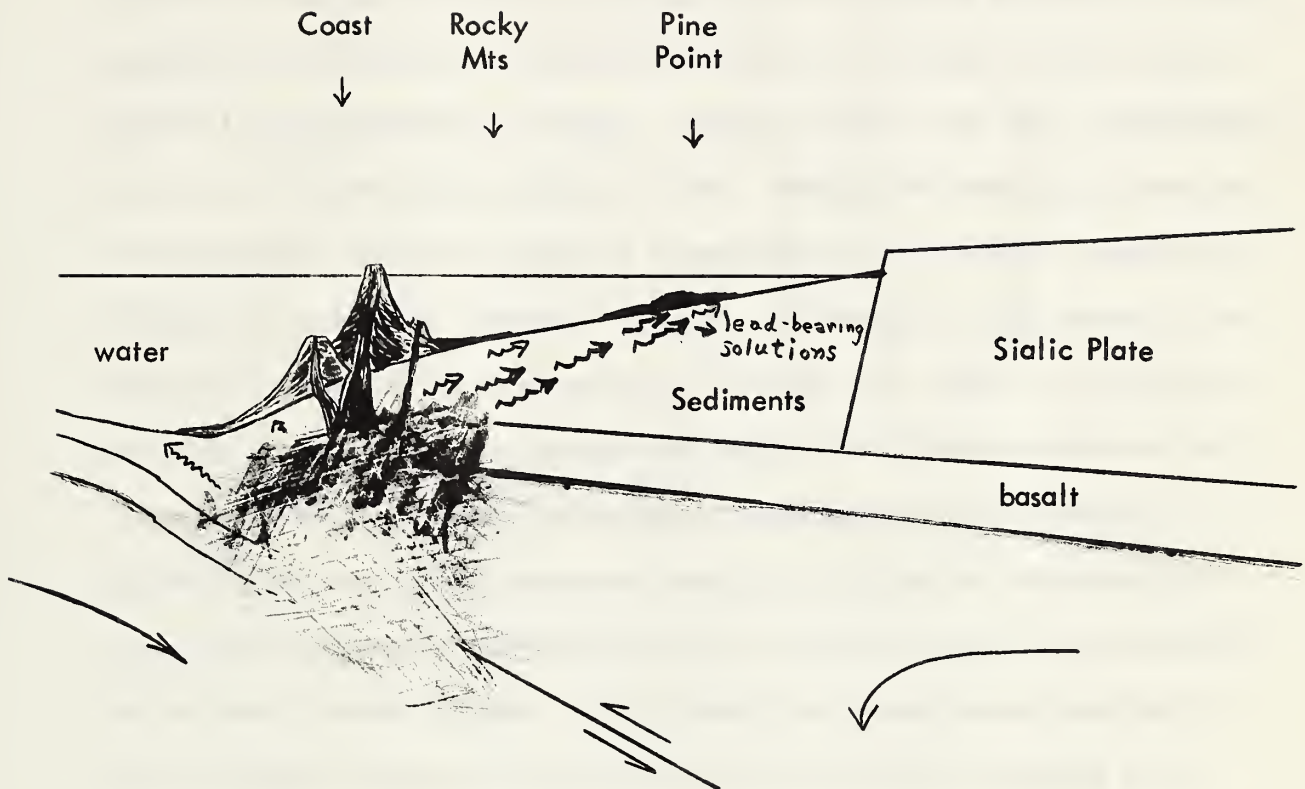












# THE WEST COAST OF NORTH AMERICA

270 MILLION YEARS AGO

(Migration of lead-bearing solutions along a fault to the surface to be deposited in a reef).



## CONCLUSION

The bulk of the data simply gives three ages, 4070, 2860 and 1550 million years. It is perfectly reasonable to adopt this simple model and stick to it. Although the 4070 million year date is a trifle early to set as the time of formation of a crustal segment one must accept the date as valid. However, one does not have to say a CRUSTAL segment formed at this time. It suffices merely to say that a heterogeneity came to exist in the upper mantle at this time. Perhaps this heterogeneity was not crustal material, but basic material of a composition more like that of basalt than of gabbro or peridotite. Instead of saying that the Mohorovicic Discontinuity constituted the surface of the Earth we say the "Conrad" did. What is most important, however, is that the basaltic material with higher  $V$ ,  $W$  than the mantle was concentrated by some mechanism and served as the nucleus for future continent growth. Such a concept is convenient because it is difficult to understand why continents would start to grow spontaneously in a particular place when the whole surface was supposedly uniform. Such a model gives geologists and geophysicists with "accepted" dates of 3300 million years as the "earliest" recordable event no reason for skepticism. The 3300 million year date still corresponds to the creation of the first crustal sialic continental segments. The stage for this construction was set 4070 million years ago. A more complicated model appears necessary to account for three samples. Its validity may only be tested by further analyses.

Although one cannot be certain from the present data, it appears highly unlikely that the Yellowknife data are consistent with an isochron between 4550 M.Y. and 2860 M.Y. It is felt that they do indeed indicate an early event in the development of the earth.

Pine Point is a vast mineralization of ordinary lead triggered by the



onset of an orogeny which added another segment (The Cordillera) to the still growing North American Continent.





## BIBLIOGRAPHY

- Kanasewich, E. R., 1963: Quantitative Interpretations of Anomalous Lead Isotope Abundances. Ph.D. Thesis, U.B.C.
- (in press): The Interpretations of Lead Isotopes and Their Geologic Significance (Radiometric Dating for Geologists). J. Wiley Ltd., 1966.
- Kanasewich, E. R., and Slawson, W. F., 1964: Precision intercomparisons of Lead Isotope Ratios. *Geochim. and Cosmochim. Acta*. Vol. 28.
- Kanasewich, E. R., 1962: Approximate Age of Tectonic Activity Using Anomalous Lead Isotopes. *Geophysical Journal of the Royal Astronomical Society*.
- Masuda, A., The Distribution of Th, U and K, and Radioactive Heat Production as a Function of Depth within the Earth. Institute for Nuclear Study, University of Tokyo.
- Russell, R. D., and Farquhar, R. M., 1960: Lead Isotopes in Geology. Interscience Publishers.



## CHAPTER V

SUGGESTIONS FOR FUTURE WORK

This thesis is only a preliminary survey of a vast area. (Average is one data point every 100,000 square miles) and it is evident that more data are needed.

1. Concentrate on the Rocks of the Yellowknife Group not only near the mines but a fair distance from them. A very precise analysis technique would be needed to analyse the sulphides (pyrite etc.) This data, if very accurate, should fall on a short-period anomalous lead isochron. This isochron is needed to see if there was an interval between the formation of the greenstones and the intrusion of the granites.
2. Pyrites present in conglomerate boulders on the greenstones of Div. A should be examined for trace leads. These should give information on a possible protocontinent which was almost completely reworked in subsequent metamorphic events. This continent could be 3300 million years old.
3. Minerals far from Yellowknife but still in Slave Province should be examined. These are important for two reasons:
  - (a) They may be used to verify whether the differentiated model is valid. If many ratios fall off the simple model *lead lines* then mixture has occurred between two ordinary leads and differentiated leads.
  - (b) Coupled with sulphur data, the lead ratios, from their positions on the *lead line*, could tell whether Churchill Province and Slave Province are essentially the same. (It appears from present data that much of Slave has been "Melted" into Churchill).
4. A field trip around Windy Point would be of great interest. It already appears as if Windy Point is a mixture of Pine Point lead and lead derived from the Shield.

As mentioned in items (1) and (2) it is important to examine minerals other than galena especially the metallic sulphides found in the metamorphosed rocks of the Yellowknife Group.



A concept of the manner in which lead can be associated with the common sulphides may be very convenient in tracing the history of an area which has undergone several periods of metamorphism. For instance, if it were known whether lead is solidly bound in the lattice of a sulphide as an integral part of the sulphide itself or is merely an intruder such as a solid solution or a mechanical mixture, then an idea of lead concentration in a sulphide as a function of the conditions of its formation can be postulated. As well, the changes in that lead concentration which might be expected if sulphides experience heating is predictable. If lead is bound in the sulphide lattice so that heating does not affect either its concentration or its isotope ratio, then the date of primary sulphide formation can be determined. If however, the lead is easily mobilized in the sulphides, then its ratios would vary under metamorphic and hydrothermal influences. It would be mixed with and contaminated by the other younger leads with different ratios. These other leads would owe their origin to non-contemporaneous magmatic intrusions, sediments derived from distant sources, or excessive crustal U-Th concentrations.

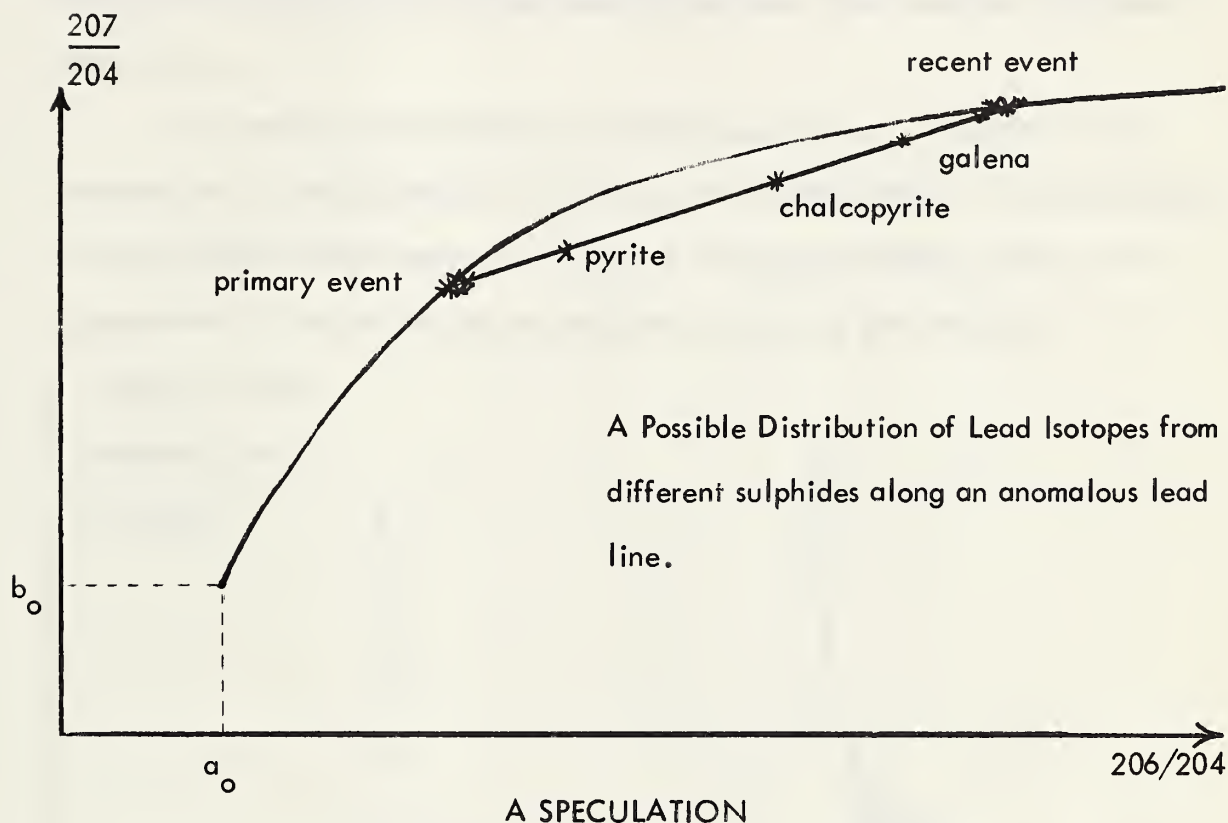
Consequently, it is necessary to obtain an idea of the thermal stability regions of the sulphides under the influence of varying degrees of metamorphism. It can then be guessed (judiciously) which sulfides will remain stable and retain their original lead ratios, and which become unstable and lose their original lead ratios; that is their "memory". Of course an idea of the concentration of lead to be expected in a sulfide is necessary too, before the feasibility of dating is known. When the problem of dating a certain metamorphosed area is faced and it is found that there are a few deposits of galena which have not been remobilized, then the possibility of dating a pyrite or an arsenopyrite might be investigated. In the case where lead in an unstable galena has become anomalous, perhaps it has remained ordinary in a pyrite or an arsenopyrite. Then the date of the most recent event may be obtained from galena, and the date of primary mineralization may be







obtained from the most stable sulphide. Lead isotope ratios from the other sulphides would fall along an anomalous lead line depending upon their thermal stability (see figure). A degree of precision would be added to the slope of the anomalous lead line and the date of an ancient event could be determined by analysis of uncontaminated leads present in stable sulphides.



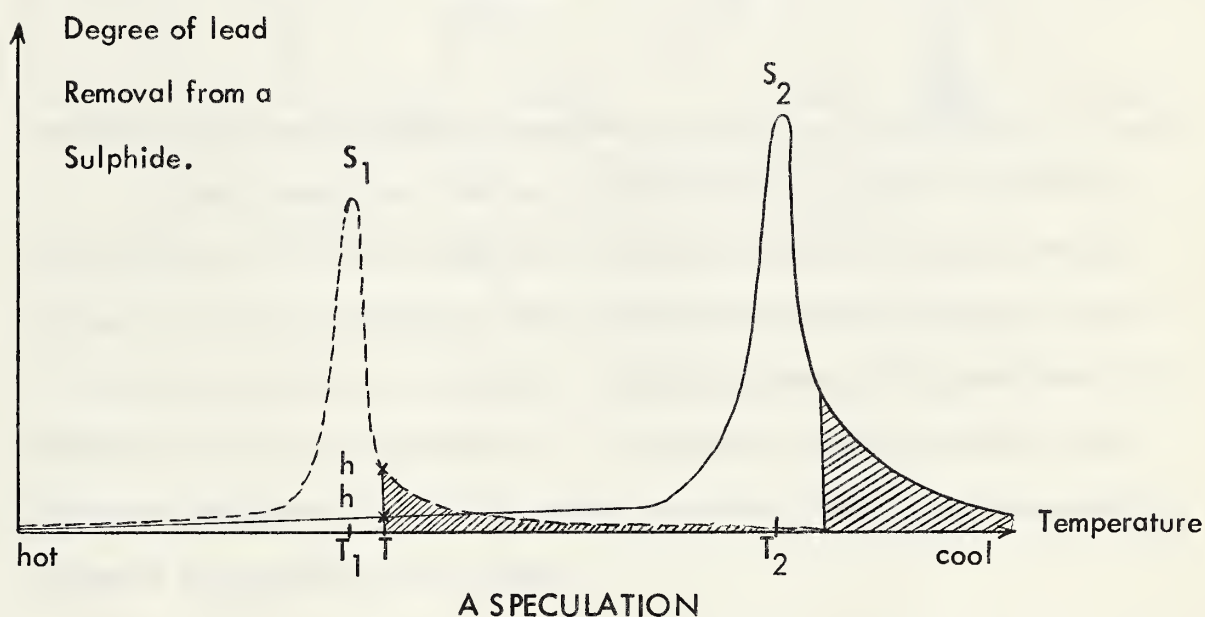
A Possible Distribution of Lead Isotopes from different sulphides along an anomalous lead line.

In view of our previous discussion it is possible that there may be lead in the cationic lattice sites of the various sulphides. Pyrite and arsenopyrite show a tendency to collect chalcophile elements, and traces of lead are common in sphalerite and chalcocopyrite. The degree of roasting necessary to remove the leads indicates that they are present in the lattice as alloys or solid solutions. Pyrrhotite, perhaps because of its different crystal structure, has a low tolerance for trace elements.



How much lead is concentrated in a sulphide? The concentration should be reasonably high (50 ppm) for an analysis to be made of the isotope ratios by the method used here. Again it is expected that the lead concentration is a function of (1) the thermal stability of galena versus the sulphide in question, (2) the affinity of the sulphide for lead, (3) the quantity of lead present in the system, and finally (4) the partition ratio of lead sulphide between other sulphides at different temperatures.

The partition ratio between crystallizing sulphides is a function of the concentration of each sulphide in the system and the temperature. The concentration of each sulphide in the system is a function of its thermal stability, which in turn is proportional to its position in the paragenetic sequence (see diagrams).

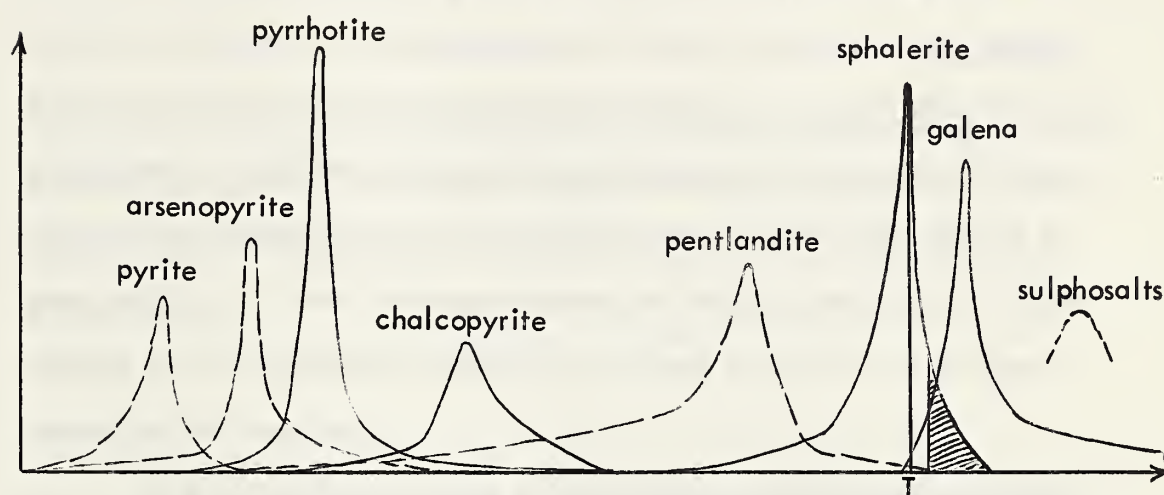


Each curve represents the degree to which a sulphide may be removed from the system by substitution, solid solution, crystallization and the like. At temperatures  $T_1$ ,  $T_2$  crystallization is the dominant process so that  $T_1$ ,  $T_2$  may be termed the crystallization temperature of sulphides  $S_1$  and  $S_2$  respectively under the conditions applying to them. The maximum height of each curve may represent the proportion of each sulphide in the system at the start of crystallization.



The shaded area indicates the region of thermal stability of the sulphide. At any temperature  $T$  the ratio of the heights of each curve  $h_1$  and  $h_2$  represents a ratio akin to the partition ratio showing the proportion and degree of association of the two sulphides.

In a similar diagram showing the zones of solidification of the sulphides the zones will be placed more or less according to the paragenetic sequence.



At any temperature  $T$  where crystallization is occurring, the partition ratio will be such that those sulphides whose stability region is farthest removed will enter into the crystallization least and those whose stability region is nearest  $T$  will enter most fully. For example, considerable galena will be associated with sphalerite but little with pentlandite. Trace amounts of lead will still be found in the high temperature sulfides, however, one reason being the high concentration of lead in the sulphide melt as a whole.

## SUMMARY

A study of the geochemistry of lead (see references at end of chapter) will give us an idea of how a lead mineral may be mineralized and the concentrations of lead to be expected in various minerals. The discussion here may give an idea of how the lead locked in various sulphides may be expected to behave under the influence of metamorphism. We have concluded that the trace





lead in the lattice of a primary metallic sulphide will remain undisturbed if the metamorphism does not exceed the thermal stability of the sulphide. Otherwise the lead will be remobilized.

This concept is of use in the analysis of lead isotopes from Slave and Churchill Provinces because it was found that two periods of extreme metamorphism have remobilized and mixed leads present in the galena samples analyzed. Memory of the earliest events is more or less erased. An analysis of the trace leads in pyrite and chalcopyrite samples, however, should produce isotope ratios which have not been affected by recent events and which represent only the PRIMARY event at which the sulphide was mineralized from its parent magma. An idea of the geochemistry of lead may also aid us in understanding in what form vast quantities of lead came up from the mantle and mineralized at Pine Point.

It is up to a future worker to analyse these sulphides and determine whether the above mentioned concept is indeed a reasonable one.





## BIBLIOGRAPHY

Agricola, 1556: DE RE Metallica, Gutenberg.

Clark, C., and Ellis, H. A., Metasomatism of the Country Near Ore Bodies and its Possible Economic Significance: Economic Geology #34 pp. 777-789.

Duffell, S., Diffusion and Its Relation to Ore Deposition. Economic Geology #32, pp. 494-519.

Goldschmidt., Geochemistry: Oxford.

Mason, B., Principles of Geochemistry.

Mason, B., and Berry. Mineralogy and Crystallography.

Rankama, K., and Sahama. Geochemistry.

Ringwood, A. E., Principles Governing Trace Element Distribution During Magmatic Crystallization. Geochim. & Cosmochim. Acta #7, pp. 189-202.

Russell, R. C., and Farquhar, R. M., Lead Isotopes in Geology.

Russell, R. D., and Stanton, R. L., Anomalous Leads and the Origin of Lead Sulphide Ores: Economic Geology #54, pp. 588.

Wedepohl., Geochemistry of Lead. Geochim. and Cosmochim. Acta #9, pp. 69-148.

Zies, E. G., Concentration of less Familiar Elements Through Igneous and Related Activity. American Journal of Science 235A, pp. 384-404.



## APPENDIX



## APPENDIX I

## THE CHEMICAL PROCEDURE USED TO PREPARE THE SAMPLES

As we noted previously there were two different types of sample analyzed - the metallic sulphides (pyrite, chalcopyrite etc.) and the lead sulphides. Naturally the galenas were the "easiest" to purify since they contained large concentrations of lead. In the first part of this section we will discuss procedures used to extract and purify leads from galenas. Then we will show the procedure used to extract lead from the other sulphides where concentrations of lead were less than one-tenth of one percent. In both cases it was found that it was easy to extract considerable amounts of lead but it was difficult to purify it so it would ionize on the mass spectrometer filament.

PURIFICATION OF GALENA

To purify the lead from galena one must start with pure reagents. Start with the following:

- 1) 2X distilled  $H_2O$  and  $HNO_3 \cdot (3N)$
- 2) Pure  $CHCl_3$  (0.00001% Pb) (Chloroform)
- 3) Pure  $NH_4OH$  (Prepare by bubbling  $NH_3$  gas through pure distilled water in a polythene flask).
- 4) 30% ammonium citrate
- 5) 10% potassium cyanide

With these reagents make up solutions of 0.1% dithyzone in  $CHCl_3$ , 0.5%  $HNO_3$ , 10%  $HNO_3$ .

Wash the dithyzone solution with one ml. of the 0.5%  $HNO_3$  then wash it three times with 20 ml. of water. Take the pure dithyzone solution and shake 20 ml. of it with the citrate solution in a separatory funnel. Drain the dithyzone from the bottom, and keep





the pure citrate solution. Do the same with KCN. (The dithyzone here will form a cyanide complex and colour the solution orange).

Now set up the equipment in a very clean lab.

### Procedure

- 1) Put a tiny cube of the galena (0.01 gm) in a beaker with 1 ml. of conc.  $\text{HNO}_3$  (3N). Evaporate to dryness. Add 20 ml. of  $\text{HNO}_3$  (1N) to the residue to dissolve it. Then add concentrated  $\text{NH}_4\text{OH}$  until the  $\text{HNO}_3$  is neutralized and the pH is 10 or more.
- 2) To the BASIC solution add 5 ml. KCN in order to hold back spurious Fe ions which may be present. (If KCN is added to an acidic solution the analyst need never worry about any solution in the future).
- 3) Pour the solution into a separatory funnel with dithyzone and shake until the dithyzone turns red. Drain off the dithyzone, add more and shake until it no longer turns red.
- 4) To the red dithyzone add one ml. of 10%  $\text{HNO}_3$  and shake in a separatory funnel until the dithyzone turns green. All the lead is now in the  $\text{HNO}_3$ . Neutralize the  $\text{HNO}_3$  with  $\text{NH}_4\text{OH}$  and return to step 2.
- 5) After repeating steps 2,3, & 4 take pure  $\text{HNO}_3$  containing the lead. Put it in a small centrifuge tube, add 5 drops of conc.  $\text{HNO}_3$  then bring to pH 4.5 by adding  $\text{NH}_4\text{OH}$ .
- 6) Bubble  $\text{H}_2\text{S}$  gas through the pH 4.5 solution. (Make sure you do this at night when there is no one around to smell this noxious gas.) A black precipitate of  $\text{PbS}$  will form ready to be loaded into the filament. It will be in a liquor of  $\text{NH}_4\text{NO}_3$ . A concentrated solution of this liquor is very important for emission so do not wash the  $\text{PbS}$ . If emission is to be good this liquor should be clear. If it is yellow or blue the sample is contaminated with iron or copper and must be repurified.



## PURIFICATION OF SULPHIDE CONTAINING TRACE LEADS

The procedure for extracting and purifying leads up to a concentration of 0.1% in sulphides is made difficult by the fact that even one part in  $10^5$  of iron in a lead extracted from  $\text{FeS}_2$  will result in failure with the mass spectrometer run. Consequently as much Fe (or Zn, Cu) must be removed as possible before a chemical extraction may be started. This is accomplished by furnace distillation of lead. A diagram of the hydrogen furnace used is shown.

The windings of the heating element of the furnace were made so that temperature is a function of the length of the furnace.

The furnace thus was to serve as a thermal lens concentrating the lead in a relatively pure state in a small area near the end. The impurities (all with higher vaporization points than  $\text{PbS}$ ) would concentrate in other areas. If an isotherm corresponding to the vaporization point of  $\text{FeS}_2$  touches the wall at point B and one corresponding to that of galena touches at point D then a ring of pyrite will form at B and one of galena will form at point D. Thermal humps at A, C, E will prevent the different sulphides from mixing and keep them from distilling as far as the galena. A furnace of "n" sections would act like a fractionation tower in an oil refinery and produce a small amount of very pure galena at the end.

### Procedure

A portion (2 gm) of the ground up sample is placed in the quartz boat. The furnace is sealed and evacuated. A flow of hydrogen is released into the furnace, and evacuated at the other end. Flow is adjusted so the pressure is 20 cm, and the furnace turned on. As the temperature increases, sulphur will be released and pumped out as  $\text{H}_2\text{S}$ . After the sample has broken down and the sulphur has been pumped out, temperature will be about  $900^\circ\text{C}$ . At this time the temperature is stabilized and hydrogen pressure reduced to 1 cm. A ring of lead will form at the end of the furnace. The furnace is moved down the tube (point A to point C) to successively redistill the lead



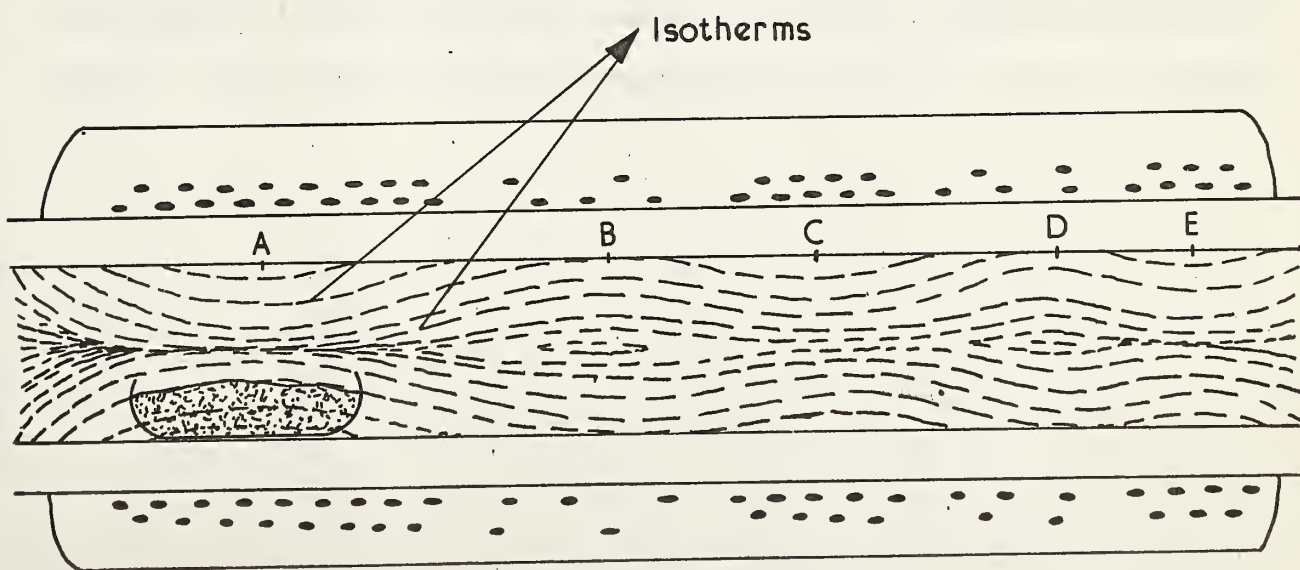
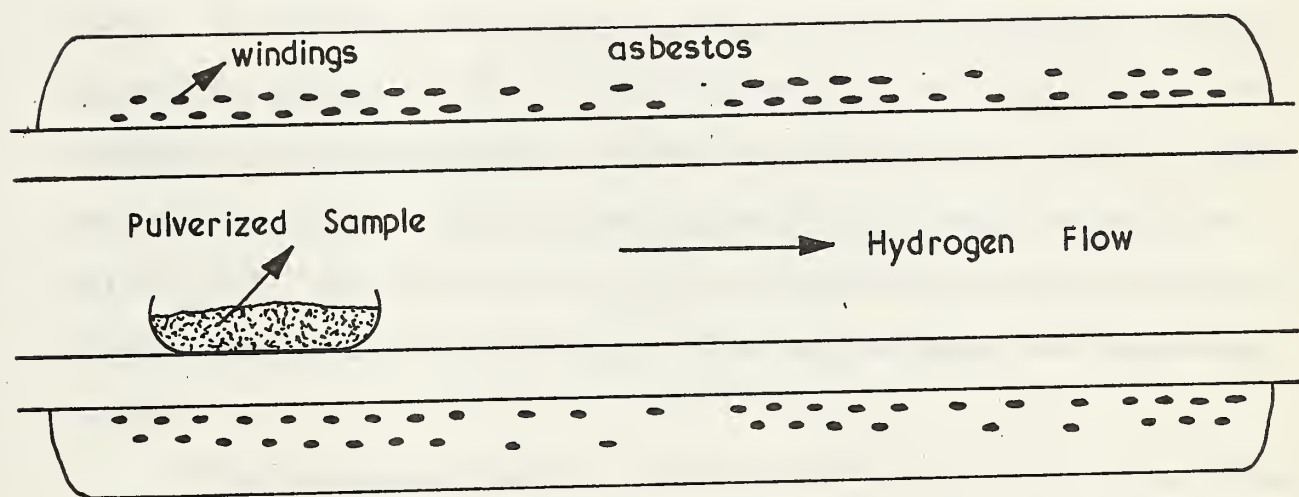
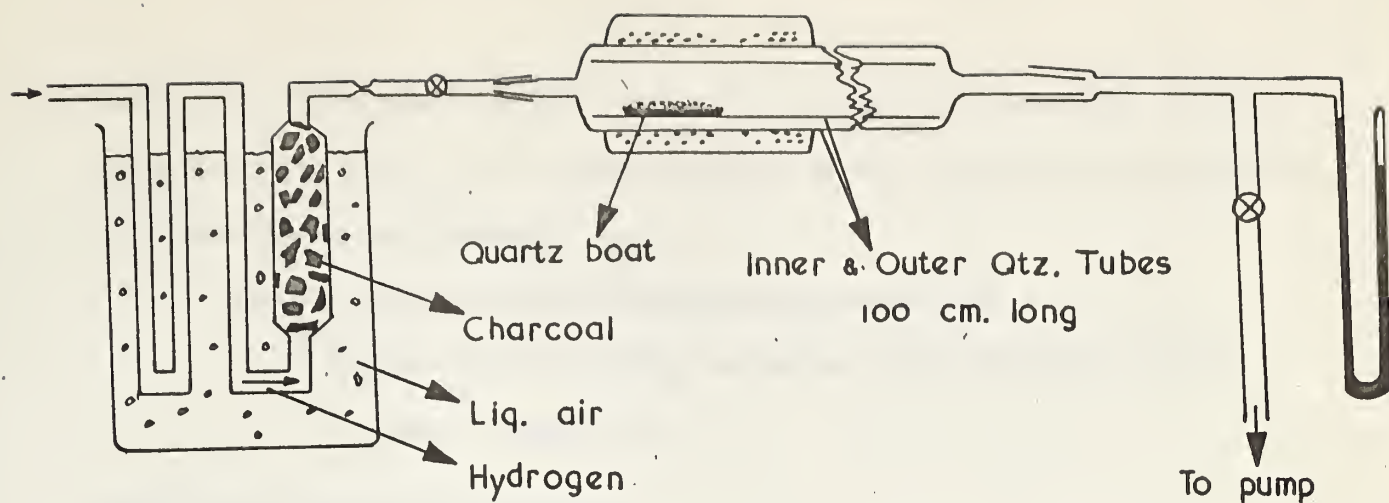


FIGURE IX The Lead Distillation Furnace





until the end of the tube is reached. The lead ring is cut off the inner tube and dissolved in purified  $\text{HNO}_3$ . At this stage one returns to Step 1 in the chemical procedure with the following modifications.

Step 3.) Extract with 0.01% dithyzone instead of 0.1%

4.) Strip with 0.5%  $\text{HNO}_3$ , and extract with 0.001% dithyzone on repeat of steps 2,3,4.

#### NOTE ON LOADING THE SAMPLE

The PbS is present as a "smear" or precipitate in the bottom of the 2 ml. centrifuge tube under a few drops of mother liquor. A drawn out capillary tube is prepared. By tapping the end of the capillary against the PbS it will break up and be forced up the tube. A small drop of PbS and liquor is ejected onto the source filament and gently evaporated to dryness. The filament current is carefully increased until a yellow ribbon of smoke curls up from the sample. Just before the smoke appears, the crystalline appearance of the sample will vanish as the sample appears to liquify (due to melting of the  $\text{NH}_4\text{NO}_3$  salt). Wait until all the  $\text{NH}_4\text{NO}_3$  has fumed off and increase the temperature slightly to make certain the salt is all gone. Then load the filament into the mass spectrometer.

When the mass spectrometer is evacuated to  $10^{-5}$  mm. put a small current through the filament (0.5 amp.) and wait until pressure is down to  $10^{-6}$  (maximum) before starting a run. There will be very little tailing if pressure is  $10^{-7}$  mm. when a run is started.





## BIBLIOGRAPHY

- Marshall, R.R. and Hess, D.C., 1960, Determination of Very Small Quantities of Lead Analytical Chemistry; Vol. 32, #8.
- Masuda, A., 1964, Experimental Method for Determination of the Isotopic Composition of Lead in Volcanics; Journal of Earth Sciences, Nagoya University, 10, 117-124.
- Ulrych, J. J., 1962, Gas-Source Mass Spectrometry of Trace Leads from Sudbury; Ph.D. Thesis.
- McCullough, H. and Krouse H. R., 1965, Application of Digital Recording to Simultaneous Collection in Mass Spectrometry; Review of Scientific Instruments, Vol. 36.



## APPENDIX II

## RUNNING OF SAMPLES - QUALITY OF RECORDS

RUNNING OF SAMPLES

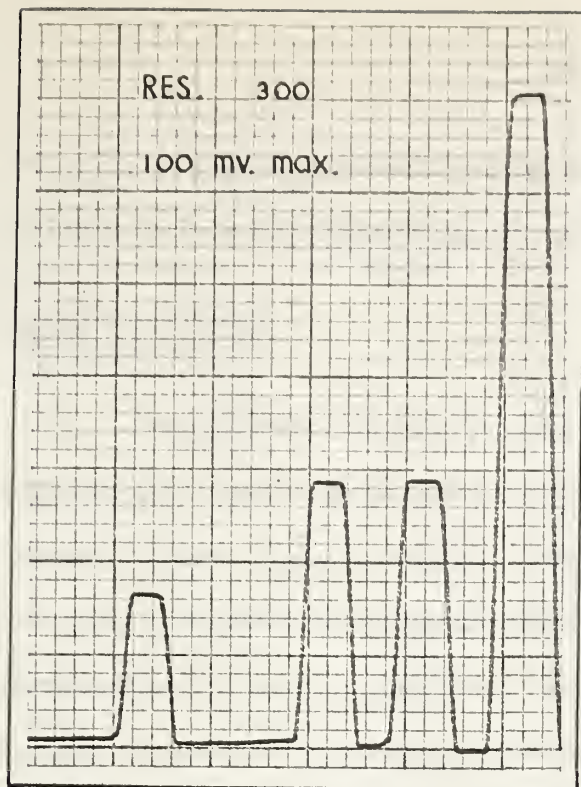
The samples were loaded as specified under "loading" in Appendix I. A procedure was adopted whereby each record was obtained under nearly identical conditions, that is, the amplifier setting, pressure, temperature, peak height, and decay (or growth) rate of each sample in each run were kept nearly the same. By running the samples under similar conditions and running the standard often, it was hoped to obtain very precise results. Precise results were obtained as well, by the use of a stable 12" mass spectrometer and a digital voltmeter to record the peak heights. The digital voltmeter printed out the peak heights to five figures and at fast scanning speed three to five numbers were printed out while the output held stable on top of each peak. The period between each "print" was one second and during this time minor variations were integrated by the digital voltmeter and the average over one second printed. Resolution was approximately 400 in the early runs but in order to obtain greater peak height was decreased to 300 by a widening of the source slits. It was considered safe to do this for pressures of  $10^{-6}$  mm., or less, since tailing was negligible.

TAILING AND PEAK SHAPES

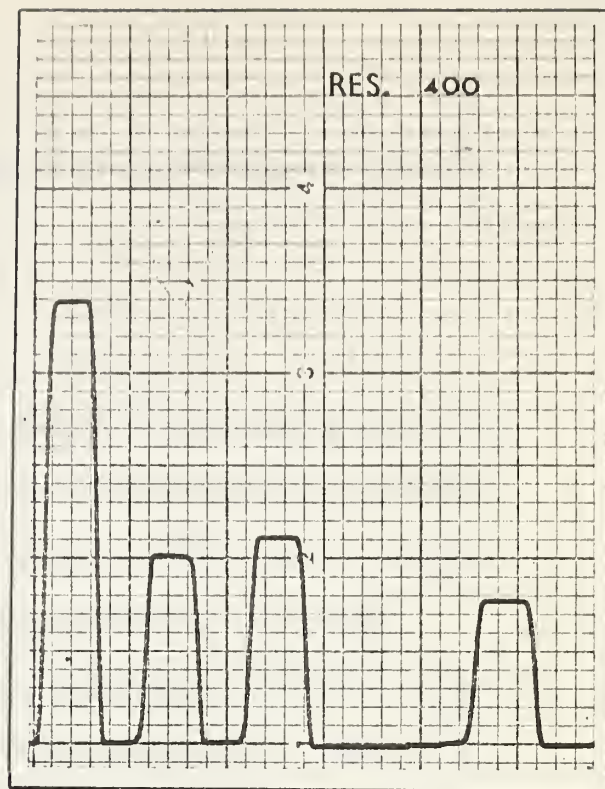
As mentioned above, the deterioration in peak shape and increase in tailing was small between records of resolution 400 (Fig. Xa) and 300 (Fig. Xb). Peak height was increased approximately four times. This was found to be necessary not so much because the sample would not emit as many ions as needed but because if it was forced to produce a high peak through narrow slits then the high concentration of evaporated particles in the source and tube ruined the peak shape (i.e. pressure increased) (Fig. Xc).





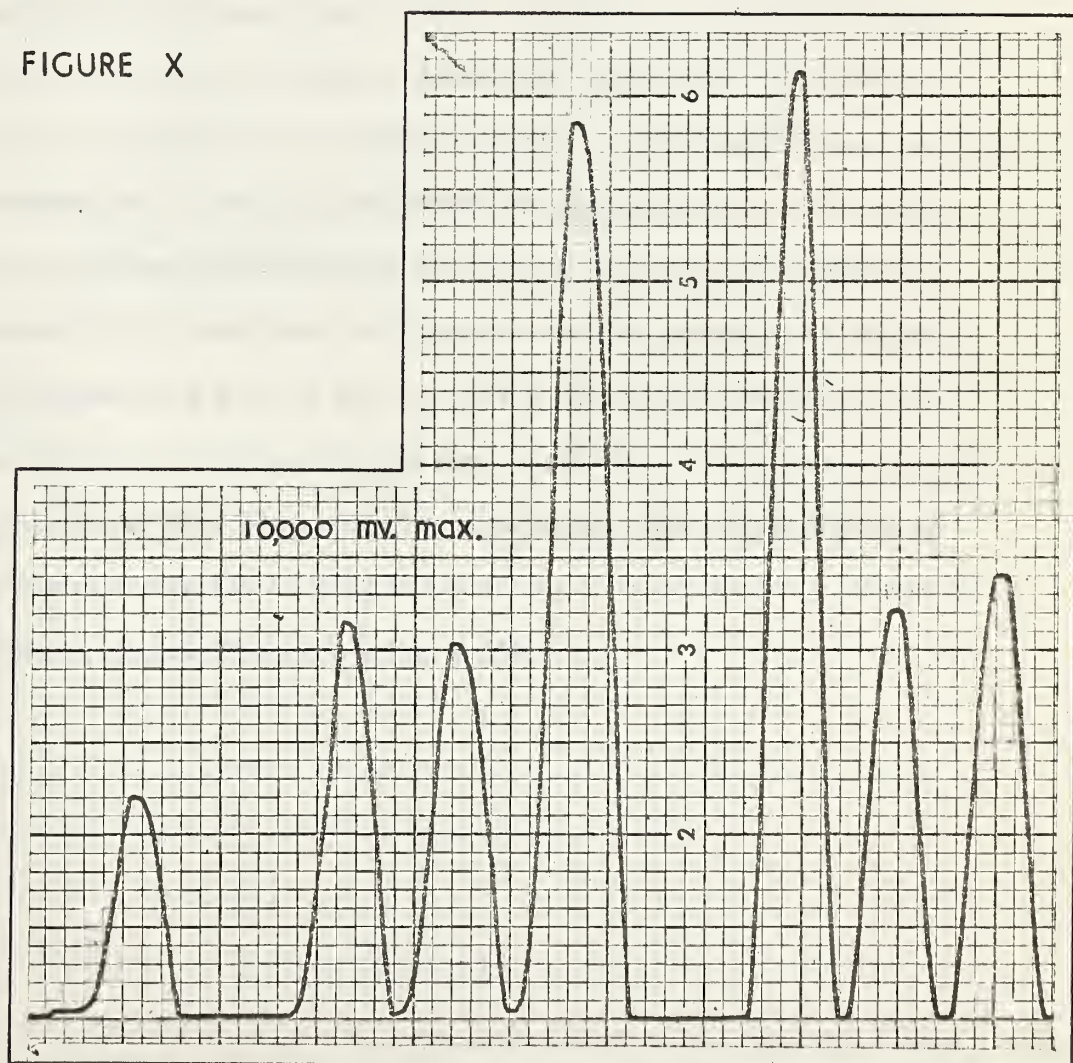


X b



X a

FIGURE X



X c





The wider slits simply allowed a greater percentage of ions in the source to reach the collector while a low pressure was maintained.

### FRACTIONATION

Fractionation occurred to a considerable extent when the samples were decaying rapidly or when an impurity (such as iron) was present and made necessary a high filament current. (refer to the Sept. 1964 runs of Standard 1003B to see the effect). However, with improved and steady emission, and very slight decay or growth, fractionation did not alter the ratios. A long record (2 hours) of the Standard was run and may be seen on the next page with the ratios shown as a function of time. This run may be considered "typical" so that the error shown would apply in general to all the runs. Notice that the standard deviation is relatively large over the whole run but is small over a period of ten minutes when the first set of peaks was recorded and a period of ten minutes when another set of peaks was recorded much later. The most important factor in error calculation was unsteady emission. The 204 peaks during the high emission characteristic of the runs were smooth on top and easy to measure accurately. There was no appreciable 204 error and thus the ratios do not fall along an errorchron. The error in this particular run is seen to be mostly in the 206/204 and not in the 207/204 primarily due to the fact that uneven emission caused a spurious 206 reading to be obtained. Consequently the error is just due to random scatter caused by unsteady emission rather than 204 error. The average may be considered close to the actual value and not amenable to being moved along an "errorchron" or a fractionation line. Therefore, reproducibility is within 0.2%.



STANDARD

Time (min.)	206/204	207/204	
0	16.138	15.669	
2	16.150	15.663	
4	16.145	15.648	Time $t_1$
6	16.153	15.644	
8	16.156	15.640	
<hr/>			
65	16.193	15.602	
67	16.254	15.680	
70	16.266	15.678'	
72	16.256	15.666	
76	16.252	15.663	Time $t_2$
79	16.238	15.653	
83	16.231	15.650	
<hr/>			
Average	16.203 $\pm$ 0.3%	15.655 $\pm$ 0.1%	

A Plot of the scatter is shown in Figure XI.

A "Typical" Spectrum

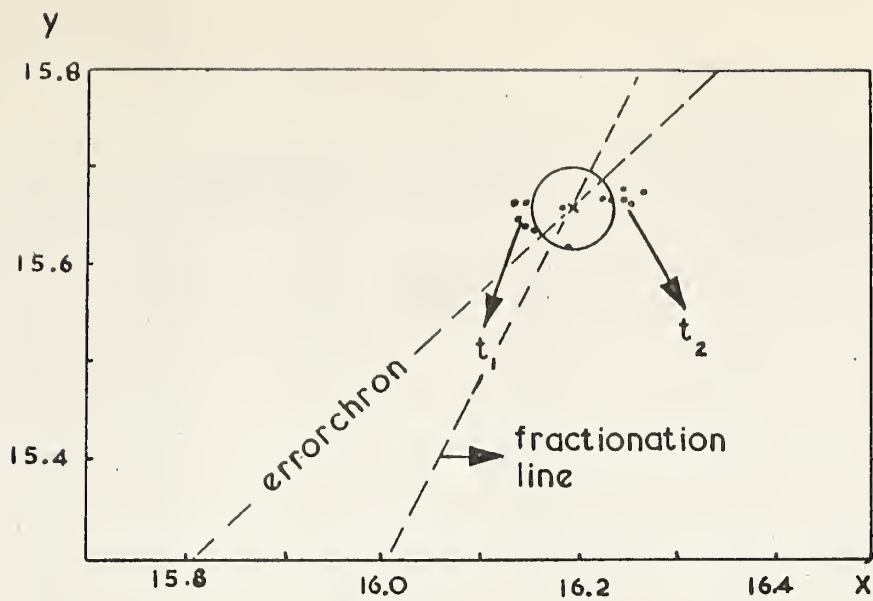
Although many experimentalists, the author included, may be tempted to pick out of literally hundred of records the only good one and label it "typical", the record shown in Figure XII may truly be labeled as such. Accompanying the peaks as recorded on the chart recorder is the record of the digital voltmeter.

Over a period of two weeks, dozens of such spectra were obtained, usually in the following sequence. "S" is the standard 1003B (Broken Hill)

S A B S C D S E F S G H S J K S

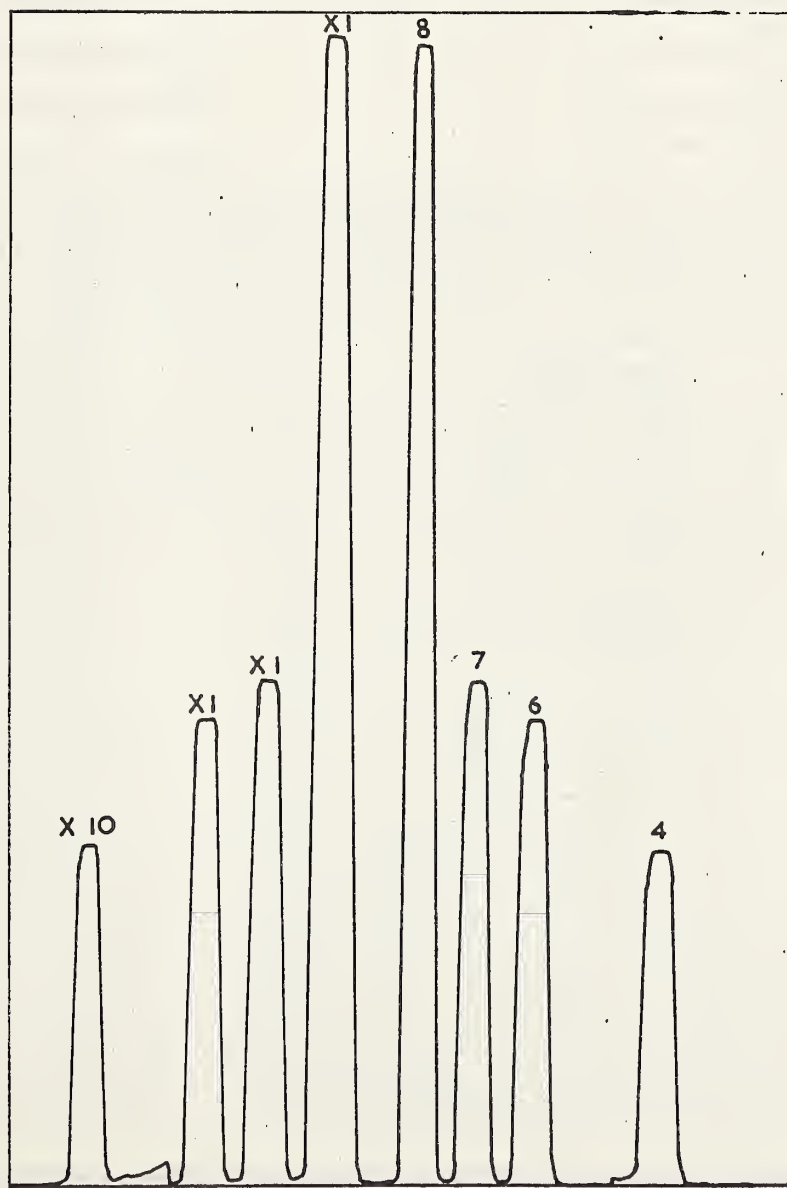
For leads found to be on a short period anomalous lead line whose ratios were





Scatter of ratios about a mean

FIGURE XI



A COMPLETE SCAN OF A TYPICAL LEAD SPECTRUM

FIGURE XII a





208 X 10

8

8

8

8

7

7

7

7

FIGURE XI b

A LEAD SPECTRUM

207 X 10

206 X 10

204 X 100

4

4

4

4

3

3

3

3

2

2

2

2

X 10

X 100





far removed from the standard S, the following sequence was run.

SASABACADAEASAS

In this case A is one of the group A, B, C, D, E. An accurate slope of the short anomalous lead line may thus be obtained. A plot showing the drift in the standard ratios with time was made and all the other ratios were adjusted to the accepted U.B.C. standard.

At the time of writing, work is in progress by Dr. H. Baadsgaard in the Geology Department to find the absolute value of S using spike techniques with  $\text{Pb}^{206}$  and  $\text{Pb}^{208}$  enriched samples of known composition.



## APPENDIX III

## METAMORPHOSED GRANITES NEAR YELLOWKNIFE

No.	Time Intruded (muscovite)	Time Metamorphosed (biotite)
59 - 18		1940
59 - 19		2070
59 - 21	2445	
22	2465	
23	2390	
24	2550	
60 - 49	2540 Prosp. LK.	
61 - 66	2615	
67	2495	
68	2555	
59 - 16		1790
17		2115
20		1880
26		1950

## METAMORPHOSED GRANITES NEAR CHURCHILL PROVINCE

## BUT STILL IN SLAVE PROVINCE

60 - 50	2485
60 - 51	2370
61 - 69	2465
61 - 70	2410
61 - 71	2465
61 - 76	2575
61 - 77	2555



## METAMORPHOSED GRANITES NEAR BEAR PROVINCE

## BUT STILL IN SLAVE PROVINCE

60 - 47	2460	1815
61 - 59		
61 - 62	2415	1755
61 - 63		
61 - 60		1905
61 - 61		2155
61 - 64	2490	
61 - 73		2100
62 - 89		1840
60 - 42		1725
62 - 90		
60 - 47	2460	1800
62 - 91	2400	1900
60 - 46		
63 - 28		1750
63 - 29		1820
63 - 30	2390	1815
63 - 31		
63 - 33	2420	
63 - 34	2365	
63 - 35	2200	
63 - 36	2310	
63 - 37		
63 - 38	2310	1995
63 - 39		
63 - 40		1865
63 - 41		2250
63 - 42		1835





## METAMORPHOSED SEDIMENTS NEAR CHURCHILL PROVINCE

60 - 52	1750
60 - 53	1750
60 - 54	1820
60 - 55	1735
60 - 56	1910
60 - 57	2000
60 - 58	1680
60 - 59	1630
61 - 72	1945
61 - 79	1780
61 - 80	1850
61 - 81	1810
61 - 84	1680
61 - 86	1880
62 - 94	1750

## METAMORPHOSED SEDIMENTS NEAR BEAR PROVINCE

60 - 40	1720
60 - 41	1720
60 - 43	1710
60 - 44	1740
60 - 46	1900 older to South
60 - 48	2175
61 - 56	1855
61 - 57	1810
61 - 65	2365



## YOUNG GRANITE INTRUSIONS NEAR PROVINCE EDGE

(cutting Snare and Great Slave Lake Groups)

60 - 42	1725
60 - 45	1850
60 - 48	2175
61 - 55	1785
61 - 58	1765
61 - 59	1815
61 - 78	1845
62 - 92	2170
63 - 32	1735

Dykes	N 70° - 80° E	(Set I)
AK 515		1830 m.y.
579		1720
583		1615
587		1655
467		1925
473		1870
584		1665
580		1750
261		2310
446		1845
450		1905
466		1615
440		2250
443		2360
518		2390

2200 - 2400 m.y.

Dykes	N 0° 0 30° E	(Set II)
AK 439		1585
465		1645
525		1965



527	1660
595	1565
474	1715

1800 - 2000 m.y.

Dykes	N 30° - 60° W	(Set IV)
AK 574		1630
575		1550
576		1460
577		1205
523		1835
531		1570
537		1265
585		1955
590		1700
592		1545

1800 - 2000 m.y.

## DIFFERENTIATED INTRUSIVE

AK 463	1925
520	2015
464	1745
497	2090
524	1490

1900 - 2100 m.y.



















**B29847**